Effect of copper and VCN addition on sintering of low alloy steel

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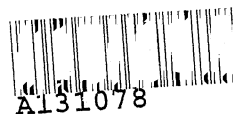
MASTER OF TECHNOLOGY

by

RANJAN

to the

DEPARTMENT OF MATERIALS AND METALLURGICAL ENGINEERING
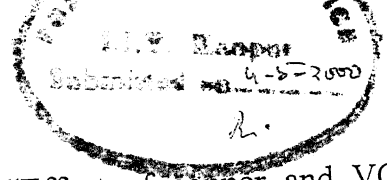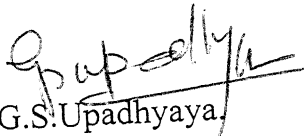
INDIAN INSTITUTE OF TECHNOLOGY, KANPUR

MAY 2000

Certificate

This is to certify that the present work entitled "Effect of copper and VCN addition on sintering of low alloy steel" by Mr. Ranjan has been carried out under my supervision and to the best of my knowledge it has not been submitted elsewhere for a degree.

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Abstract

Copper is invariably added to P/M steels to serve one purpose or the other. It compensates for shrinkage and promotes liquid phase formation during sintering apart from strengthening effects. It also improves hardenability of P/M steels.

In the present study, copper and vanadium carbonitride (VCN) were added to low alloy P/M steel and their effects on the densification behaviour and mechanical properties were studied. The effect of heat treatment was also studied. All the sintering were carried out at 1120 °C for one hour in hydrogen atmosphere. For heat treatment, the samples were austenitized at 1000 °C for 10 minutes and then oil quenched to room temperature.

The increase in carbon level in steel from 0.3 % to 0.5 % resulted in better densification and better mechanical properties. The results showed that, although copper addition resulted in poor densification, it improved mechanical properties of the steel. Further improvement was observed after heat treatment. The best results were observed for 10 % copper - 0 % VCN composition.

VCN addition did not help either in densification or in improving mechanical properties. But when added simultaneously with copper, it affected the densification behaviour of the steel.

Acknowledgment

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Literature Review

1.1 Introduction

Low Alloy steels constitute a category of ferrous materials which exhibit properties superior to plain carbon steels for the same carbon content. It is due to addition of some alloying elements such as Nickel, Chromium and Molybdenum. As the name suggests the total alloying element content is kept in the range of 2.07% to the levels just below that of stainless steels which contain a minimum of 10% chromium. The total carbon content ranges from less than 0.1% to 0.55%. [1]. The primary function of these alloying additions is to increase the hardenability in order to optimize mechanical properties and toughness after heat treatment as most of these steels from this category are used after heat treatment. [1,4]. In other cases however alloying addition is done to prevent environmental degradation under certain special service conditions. [1,3]. The most important use of these steels is as structural steels. Their present usage ranges from oil and gas pipeline to storage tank and from earth moving equipment to complicated automobile parts. [2,6].

High strength low alloy steels or HSLA steels as they are popularly known as, is a classification of low alloy steels. In these steels strength is of

prime importance. Technological advances in last few decades such as welding, low temperature uses, high pressure utilities etc. which require some better properties than the conventional steels have ushered in the development of these steels. The microstructure of these steels consists of ferrite as primary phase along with pearlite or tempered martensite or tempered bainite etc. as second phase. However presence of pearlite is avoided or limited as it has detrimental effect on the impact transition temperature of the steel and it increases work hardening in them (Figure: 1.1). [2,4,6].

Micro alloyed steels are another classification of low alloy steels and it falls in the category of HSLA steels. As the name suggests the total content of micro alloying elements in these steels is limited to the order of 10^{-1} % while providing mechanical properties equivalent to the conventional HSLA steels. [5,6]. Carbon content in these steels is still lower, e.g. < 0.1%. [4]. According to accepted view, only eight elements are considered as micro alloying elements in steels.They are further classified into three sub-groups as [5]:

- Metals having strong tendency to form carbides or nitrides or carbo- nitrides. These metals are Aluminium, Titanium, Niobium and Vanadium.

- Non-metallic alloying additions. They are Boron and Phosphorus.

- Inclusion especially sulphides shape controlling elements. These are Tellurium and Zirconium.

Some other elements too are being tried as micro alloying elements such as Molybdenum, Chromium, Cobalt etc. [26,48,49]. It is expected that all the micro alloying additions are present in some combined state e.g. as carbide or nitride or carbo-nitride. Some times borides and phosphides too may be present but they are not added with this intent. [32]. Strength in micro alloyed steels is provided by precipitation hardening effect and grain refinement. But both these properties are dependent on the precipitation of carbide or nitride or carbo-nitride particles. [6]. Micro alloying additions often bring down impact transition temperature of the steels (Figure: 1.2). [2].

1.2 P/M low alloyed steels

In production of low alloyed steels through P/M the general approach is to work with an iron based system, which after sintering results in better-sintered properties. The most general approach is to enhance the sintered density. Good results have been obtained in this approach by liquid phase sintering. [7]. Some researchers have tried to produce such P/M steels through solid state sintering too (Figure-1.3). [8]. Some approaches to produce P/M low alloy steels are [9]:

- Starting with elemental powders or powders of master alloys. This approach is common for simple binary systems such as Fe-Cu, Fe- Ni, Fe-Co, etc.

- Starting with diffusion bonded partially pre-alloyed powders where P/M components require higher compressibility and strength.

- Iron powders coated with alloying elements using hydro-metallurical methods or electro-deposition techniques, which render the powder very costly and uneconomical. These powders are used for very special purpose only.

- Starting with pre-alloyed powders, which are produced by atomisation of molten iron to which prior alloying addition is done. But these powders are less compressible.

      Copper is one of the most important alloying elements in P/M low alloy steels. It is added to almost every steel system for some purpose or other. Some of the most common and important P/M steel systems are discussed in this section.

1.2.1 Fe-Cu system

      Fe-Cu system is one of the most studied systems in P/M. Being one of the earliest known systems undergoing liquid phase sintering, a lot of research have been done on this system. Some of the most prominent observations made regarding this system are listed below:

- This system shows dimensional growth with increase in copper content up to 8%. [11,33].

- The extent of dimensional growth is a function of sintering time, sintering temperature, green compaction pressure and heating rate. [7,12,13,19].

- The dimensional growth depends up on powder character such as particle size of iron and copper powder, presence of internal porosity, method of production, grain size etc. [2,7,13,14,19].

- Swelling characteristics of Fe-Cu compacts are affected by addition of alloying elements such as carbon, nickel etc. [7].

Mechanical properties of Fe-Cu compacts depend upon cooling rate [15] and post-sintering operations such as aging etc. Sintering behavior of compacts depends significantly up on the total copper content. It is different for copper content less than 5 % and for more than 10%. This is due to the differences in the amount and duration of liquid phase present during sintering. [18]. This may be attributed to the fact that in the former case transient liquid phase sintering occurs while in the latter case persistent liquid phase occurs. [19]. The homogeneity of copper and iron in the system increases with increasing copper content. [16]. It depends upon particle size of copper too. It is believed that 40% liquid is required for rearrangement of particles to start. But homogenization may not complete even after long sintering time. [7].

Copper growth has been studied a lot and various mechanisms have been proposed to explain this behavior. The two most common are i) Diffusion

mechanism, and ii) Penetration theory. [9,14,18,21,24]. The diffusion mechanism proposes expansion of iron lattice due to solid solution of copper and this is the cause of growth in compacts. The maximum growth is therefore expected at 8% copper content, as it is the solubility limit of copper in austenite. But the rate and the magnitude of growth during sintering cannot be accounted by this theory alone even if the maximum expansion limit defined by it is true. [9,14,18,21,24].

The penetration theory proposes that liquid copper penetrates along the grain boundaries of iron particles and separates them apart causing dimensional growth in the compact. However, now it is accepted that total growth in Fe-Cu compacts during sintering is a result of combined effect of four mechanisms acting simultaneously. [7]. They are:

- Penetration of melt between iron particles.

- Penetration of melt along grain boundaries.

- Diffusion of copper into iron from particle surface.

- Diffusion of copper into iron particles from grain boundaries.

While the penetration of copper melt between particles is the result of surface energy considerations and capillary forces, the penetration of melt along the grain boundaries depends upon the dihedral angle considerations. Sintering cycles too affect the dimensional growth behavior of Fe-Cu compacts. Sintering carried out with a hold provided at ferrite-austenite

transformation temperature results in less expansion than the case where sintering is done continuously. This may be either due to substantial copper diffusion during hold period or due to formation of some iron skeleton during the hold (Figure: 1.4).

Some theoretical explanations too have been provided for expansion rate during sintering of Fe-Cu compacts. The system undergoes little expansion up to 700 °C and above this temperature the rate of expansion is large. Change of phase from ferrite to austenite too affects the rate of expansion. The phase change, which occurs at around 900 °C, abruptly decreases the expansion rate. It is because of enhanced solubility of copper in austenite. In fact prolonged sintering at a temperature just below the peritectic temperature results in very less expansion. [7]. It is observed that compacts produced from pre-alloyed powder show relatively less copper growth. The extent of this growth depends on the degree of saturation of iron powder with copper. [7]. In fact shrinkage is reported in Fe-Cu compacts produced from carbonyl powder coated with copper. This compact has excellent mechanical properties but the cost of production is very high and makes this approach uneconomical. [20].

Rate of cooling from sintering temperature to room temperature affects the mechanical properties of the sintered compacts. Fast cooling rate results in stronger alloy. One possible explanation for this is prevention of copper

segregation during cooling. Since the cooling rate is too fast copper could not grow into large precipitates. During slow cooling copper grows into larger precipitates and these precipitates adversely affect mechanical properties. [20]. Other explanation could be the precipitation of very fine copper precipitates in ferrite matrix during rapid cooling. [15]. Sometimes sintered Fe-Cu compacts are aged at some elevated temperature to get better properties. Hardness after aging increases with increasing copper content up to 8-10%. This is because of increase in number density of precipitates and decrease in their size. [16]. Aging time to attain maximum hardness decreases with increasing copper content. [17].

Infiltration of iron P/M part by molten copper is another technique to produce Fe-Cu P/M parts. Molten copper is carried into inter-connected pore channels of the P/M parts by capillary action. Compacts produced by this method have good impact and fatigue properties.

1.2.2 Fe-Cu-C system

Carbon is often added to Fe-Cu system for various reasons. One of the main reasons is to compensate for the growth during sintering caused by the presence of copper. Other reasons include prevention of decarburisation of Fe-C system and increase in strength and hardness of the sintered compacts. Carbon addition provides economical edge over the sintering of Fe-Cu binary alloys as it reduces cost of post sintering machining operation. Sintering atmosphere plays

an important role in deciding the properties of sintered compacts (Figure: 1.5 and 1.6).

Various approaches have been suggested for understanding the effect of carbon addition into Fe-Cu system. One approach is to explain it on the basis of normal liquid phase sintering mechanism where a ternary liquid phase forms at 1095 C. but this approach is not very accepted as the stability of this liquid is suspected. Other approach is to explain the phenomenon of decreasing growth with increasing carbon content in the system. This is based upon the dihedral angle considerations. It is found that the dihedral angle between copper rich melt and austenite increases due to addition of carbon in the system (Figure: 1.7). For low dihedral angle the melt spreads through the pore channel and forms a thin layer around iron particles and thus covers a large area for diffusing into iron. But with the addition of carbon into the system, this dihedral angle increases. Due to this copper could not flow into pore channels and remains either at grain boundaries or at it original site. [24]. Another approach is to explain the phenomenon using diffusion. According to this, almost all carbon is dissolved into iron before diffusion of copper starts and the presence of this carbon prevents diffusion of copper into iron. The increase in shrinkage with increase in carbon content may be attributed to the increase in self-diffusion coefficient of austenite. [11].

The swelling in Fe-Cu-C compacts can be made negligible by using elemental iron powder produced by atomisation or some other processes along with appropriate copper and carbon addition. In fact shrinkage is found in compacts made from carbonyl iron powder. Increase in surface area results in decreased swelling. It also results in reduced amount of pearlite in the sintered compact, which may be due to increased oxygen content in the system. Pore size in the sintered compacts too is decreased. [11]. The best dimensional stability is observed in the case of partially pre-alloyed powder. The role of ternary liquid phase becomes important in this context. But the stability of this liquid phase is still suspected. [7,11]

Atmosphere control is important in the case of sintering of Fe-Cu-C P/M steels. It is due to the presence of carbon that may be lost due to decarburisation during sintering. Presence of moisture in the sintering atmosphere results in increased decarburisation from the surface. It often results in carbon concentration gradient in the sintered compacts. [7]. The swelling characteristic of the compacts too is affected by sintering atmosphere. In fact these two effects are inter-related. The carbon if completely diffused into iron before the diffusion of copper starts prevents swelling of the compacts. But if the same carbon is lost due to decarburisation during sintering the copper growth is increased. Since decarburisation is less in atmosphere containing H_2 and CO

(both) or moisture the extent of swelling is relatively less in these sintering atmospheres. However swelling is not much affected by sintering in N_2 or endo gas atmosphere. [7,35,38]

Fe-Cu-C sintered components respond well to post sintering heat treatment. Heat treatment is done to almost all low alloy P/M steels to improve their properties such as strength and toughness. These heat treatments induce some microstructural changes. They promote the proportion of martensite and reduce the fraction of pearlite. The most common treatment includes austenitisation of P/M part in the temperature of 870-1000 ^{0}C for some time followed by quenching in oil or water. Then the parts are tempered in the temperature range of 300-500 ^{0}C for some time. This is done to increase their toughness. The fraction of pearlite is minimized but it cannot be reduced to zero because of the presence of pores. Some pearlite is always found near pores because of decreased thermal conductivity there. Due to this critical cooling rate cannot be achieved in those areas. [7,22].

Like Fe-Cu system, copper can be infiltrated into Fe-C P/M alloys to get materials with good strength and hardness with better dimensional control.

1.2.3 Copper in complex steels

Complex steels mean steels that contain more than one alloying element in substantial amount. Copper is added to almost all such P/M steels.

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The most common purpose for the addition is to compensate for the shrinkage encountered during sintering when done without copper. It is also added to promote liquid phase sintering for better densification and faster sintering wherever required. Apart from these copper also contributes in the strengthening of steels. [1]. The role of copper in some common P/M steels is discussed here.

1.2.3.1 Copper in sintered Ni-steels

Adding a little copper compensates the shrinkage found during the sintering of Fe-Ni-C steels. But the effect is limited to the case when copper content is limited to approximately 2%. The steel thus produced has much better mechanical properties as the copper has more solubility in iron and hence effect on the properties of steels (Figure: 1.8). [7,40].

1.2.3.2 Copper in sintered Ni-Mo steels

These steels have very good hardenability due to the presence of molybdenum. Hence with addition of copper the strength of these steels increases tremendously. Copper also helps in promoting liquid phase sintering in the system. The homogeneity in the steel is a problem as all the three alloying elements have small diffusion rate in iron. The powder characteristics especially that of iron is important as surface morphology of particles affect diffusion controlled distribution. Other alloying elements, their amount ant powder characteristics too affect the sintered properties. Fine and pre-alloyed powder is preferred to control copper growth. Atomised copper powder causes less

swelling and hence preferred. Ready to use P/M parts can also be produced by carefully controlling composition and cooling rate after sintering. These P/M parts can also be carburised. [7].

1.3.3 Copper in sintered Mn-steels

Copper in this system is added for providing dimensional stability and with normal manganese content the amount of copper required is approximately 2%. The common trend in P/M production of these steels is to use ferro-manganese pre-alloyed powder along with elemental copper and graphite powder. But homogenization is a problem in this case as Fe-Cu melt forms before manganese is completely diffused in iron and renders further diffusion difficult. So the use of MnCu pre-alloyed powder along with iron and graphite is preferable.

1.2.3.4 Copper in sintered Ni-Mn steels

P/M Ni-Mn steels are generally used as a replacement of P/M Mn steels. Since, homogenization of manganese in iron is difficult during sintering due to presence of Fe-Cu melt, a little nickel is added to the system. This helps in homogenization of manganese as well as nickel. Due to better homogenization of alloying elements the mechanical properties of these steels are better. [7].

1.2.3.5 Copper in sintered Ni-Mo-Mn steels

Copper increases hardenability of Ni-Mo-Mn P/M steels. It modifies their microstructure to produce complete martensitic microstructure which otherwise contains ferrite as well as pearlite even after heat treatment. Copper addition in these steels facilitates better homogeneity and improves their strength and hardness without affecting ductility. [42].

1.2.3.6 Copper in phosphorus containing steels

In this case copper and phosphorus form a low temperature eutectic and hence liquid phase sintering occurs at a lower temperature. Here dimensional change is not a function of carbon content and hence production of low carbon P/M part with very good toughness is possible. Copper also increases hardness and strength but only at the cost of ductility. [43].

1.2.3.7 Copper in sintered B-steels

P/M steels containing boron and carbon can be directly used without post sintering heat treatment. This needs careful control of composition. Mechanical properties of these steels are very good, may be due to persistent liquid phase (Fe-Cu-B-C ternary) sintering resulting in very good densification. Infiltration of copper into boron steels results in better impact and tensile properties. Dimensional stability too is good primarily because boron diffuses into iron along with carbon and thus preventing copper growth (Figure: 1.9). [7].

1.2.3.8 Copper in other sintered steels

Copper is often added to MnS containing P/M steels to improve their machinability. [44].

Copper is added to tellurium containing P/M steels to prevent tellurium loss during sintering. Apart from this it also improves their strength and machinability along with dimensional stability. [44].

1.3 Role of vanadium in P/M steel

Conventionally vanadium is regarded as one of the micro-alloying elements. [5]. It is being used as a micro-alloying element since last few decades either individually or in combination with niobium. [2]. In case of normal addition vanadium is a ferrite stabilizer with limited solubility in austenite that too in the presence of carbon. It shows age hardening tendency in ferrite. It is a strong carbide and nitride former. It increases hardenability of steels as it acts as grain refining agent. Its carbides and nitrides play important role during micro alloying as they cause grain refinement and precipitation hardening (Figure: 1.10). [2,47,48,49]. Vanadium also improves toughness by stabilizing dissolved nitrogen in steels. The impact transition temperature of steel increases when vanadium is added. [53].

VC and VN are the most important compounds that make vanadium useful in steels. During micro alloying VC and VN precipitate out. Of

all the carbide forming elements vanadium forms special carbide. It is so because its carbide dissolves completely into austenite at a temperature as low as 900 ^{0}C (Figure: 1.11). But it precipitates out once the temperature is lowered because VC has negligible solubility in ferrite. In wrought micro alloyed steels, an optimum level of precipitation strengthening occurs at a cooling rate of about 170 ^{0}C/min when V(C,N) particles precipitate. At cooling lower than this rate, precipitates coarsen and are less effective for strengthening. At higher cooling rates more V(C,N) remains in solution and thus a smaller fraction of V(C,N) precipitate. Hence precipitation strengthening is reduced. Manganese content and ferrite grain size also affect the strengthening of vanadium micro alloyed steels. [54]. This property renders vanadium micro-alloyed steels ability to get normalized at a much lower temperature than other micro-alloyed steels. VC simultaneously strengthens inter-lameller ferrite in pearlite too in the same fashion. [50]

Vanadium containing low alloy steels are produced through powder metallurgy too. The most significant such P/M steel system is Mo-Cr-Mn steels where vanadium is introduced to promote better hardenability. Production of low alloy vanadium containing P/M steel is done by different techniques. Most common technique is to use elemental vanadium. [31]. In a recently

developed method vanadium is introduced in the system through a master alloy. The part shows better properties in the latter case. [51]

1.5 Factors affecting the properties of sintered ferrous compacts

Properties of sintered P/M steels depend upon a lot of parameters, materials as well as process. Some of those parameters are described in this section.

1.5.1 Particle size

The extent of densification is highly affected by particle size and shape. For example, in case of Fe-B system, 0.3% boron is sufficient to densify carbonyl iron powder up to 99.8% while more than 1% boron is required to produce 99% dense iron from atomized powder.

If initial powder is coarse the densification extent of the steel depends upon initial distribution of powders of alloying addition and the matrix i.e.; the mixing of powder becomes important. But if the powders are of intermediate range the rearrangement of particles during isothermal process and solution-reprecipitation during other period become important. [5,29]

1.5.2 Green compaction pressure

Application of higher green compaction pressure may inhibit the liquid phase distribution, as the pore channels in the green body become

narrower. And the already narrowed channels are quickly closed by solidification of non-equilibrium melt at the sintering temperature. Thus large agglomerates of solidified undistributed eutectic may be present along with unaffected pores causing deteriorated sintered properties. [28]

1.5.3 Sintering temperature

Increased sintering temperature means increased rate of material transport resulting in favorable properties up to certain extent. Thus high sintering temperature results in better densification as well as in better homogenization of microstructure and hence better mechanical properties e.g., strength, hardness, etc. But higher sintering temperature may result in pore coarsening as well as grain growth, which detrimentally affect the sintered properties. Formation as well as coarsening of secondary pores may occur which affect the dimensional stability of the parts which are already affected by the copper growth problem as almost all low alloy P/M steels contain copper. Hence sintering temperature should be selected carefully to optimize the effects. [27,28,34]

1.5.4 Sintering time

Similar to increase in sintering temperature increased sintering time results in increased volume of material transported. Increase in sintering time results in better mechanical properties up to an extent due to improved bonding,

pore rounding and better homogenization. But increased time may lead to grain as well as pore coarsening deteriorating the mechanical properties. Increased sintering time mostly affects mechanical properties rather than density of sintered compacts. Sintering time is decided in conjunction with sintering temperature. [34].

1.5.5 Powder composition

In most of the cases a mixture of pre-alloyed and elemental powder or partially pre-alloyed powder is used. Fully pre-alloyed powders are hard and less compressible and hence result in more tool wear. Therefore, they are avoided (Figure: 1.12). [26]. In case of only elemental powder complete homogenization is difficult. The presence of some elements such as molybdenum which has low diffusivity in iron may further deteriorate product quality. Using molybdenum in elemental state is difficult also because it is easily carburised to Mo_2C or Mo_6C or $Mo_{23}C$. The liquid phase form at a temperature of 1230 ^0C, hence low temperature sintering is also difficult. However no such problem is encountered in the case of pre-alloyed powder as alloying additions are already homogenized. Therefore they result in better sintered properties.

1.5.6 Sintering atmosphere

Atmosphere during the sintering of low alloy P/M steels is very important as the possibility of carbon loss is always there. Low alloy steels are generally sintered in a reducing atmosphere such as hydrogen or cracked ammonia to prevent oxidation of powder during sintering. The presence of moisture is avoided as it results in decarburisation. Some other sintering atmospheres are nitrogen, endo gas, nitrogen diluted endo gas etc. Vacuum does not offer any substantial advantage and hence seldom used. [7,10].

1.5.7 Post sintering operations

Further increase in the mechanical properties of low alloy P/M steels can be achieved by heat treatment. The aim of these heat treatments is to get desired microstructures. A complete martensitic microstructure is the most desirable one. Sometimes alloy composition or production route is manipulated to achieve this. [30]. The most common heat treatment is austenitizing followed by oil or quenching and then tempering to induce toughness. Austanitizing and tempering temperatures depend upon the composition of steels and they are selected to optimize the desired properties. In case of steels containing very small amount of carbon the effect of tempering is not significant. However some aging is observed due to precipitation of small copper particles, when these compacts are tempered after quenching. [22].

1.5 Scope of the present work

Fe-Cu systems constitute one of the most popular systems in the ferrous P/M materials. In binary Fe-Cu P/M alloys the compact shows some swelling during sintering, the extent of which increases with the amount of copper content up to a limit (approximately 8%) in the system. The most common approach in P/M to prevent copper growth is to add some carbon into the system. Though dimensional stability is achieved in the sintered compacts the problem of micro-structural inhomogeneity arises as copper segregates at grain boundaries or at its original site. The problem increases with increasing carbon or copper content. A lot of other alloying additions have been made in Fe-Cu-C system to produce P/M materials with desired mechanical properties as well as dimensional stability.

Vanadium is an important alloying addition in wrought steel though it is added as micro constituent. Mechanisms of action of vanadium in improving properties of steels have been studied and are accepted as due to precipitation hardening induced by fine precipitates of VC and VN and grain refinement. The special properties of vanadium which help in inducing these properties are:

* High affinity of vanadium for carbon and nitrogen.

* Solubility of VC and, up to some extent, of VN into austenite but not in ferrite.

The aim of this work is to study the effect of vanadium carbonitride addition in copper bearing P/M steels. Since vanadium induces hardening in the form of VC and VN, in the present study their solid solution i.e., V(C,N) is used. The effects of varying V(C,N) as well as copper contents on the densification characteristics are studied.
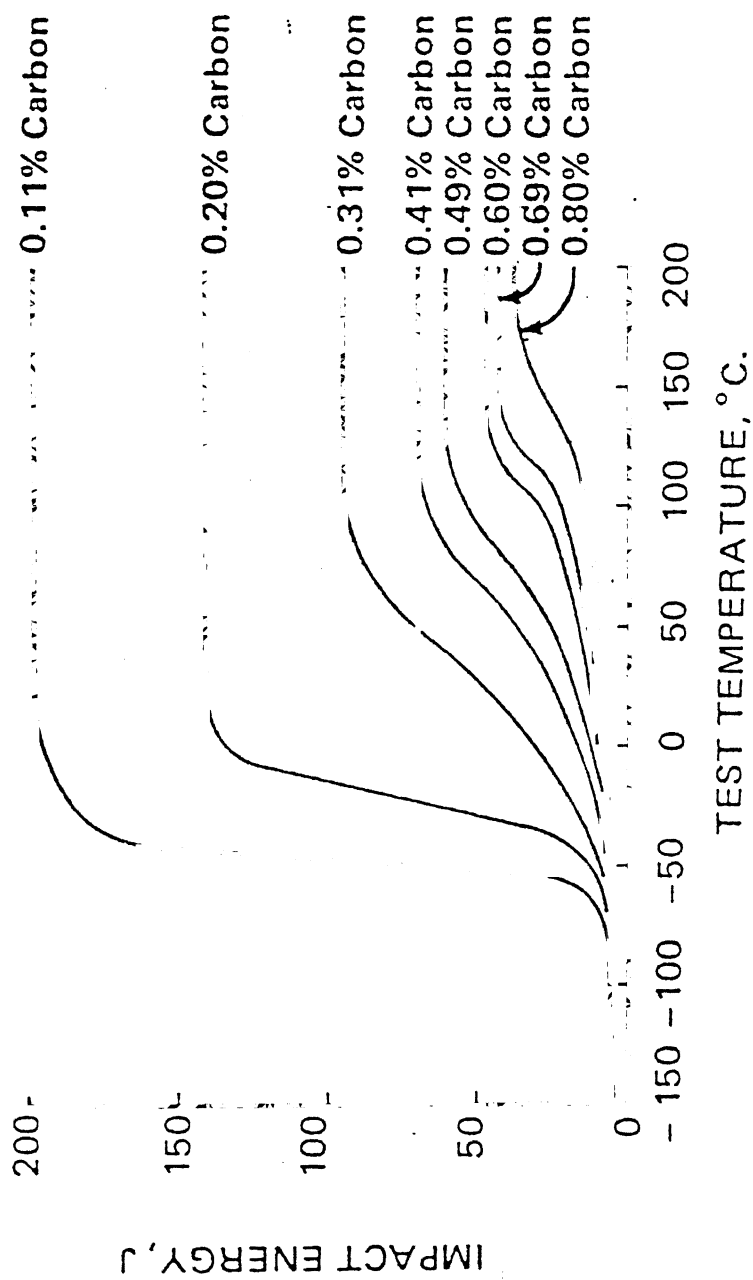
Figure 1.1: The effect of carbon and hence the pearlite content on impact transition temperature curves of ferrite-pearlite steels. [6].
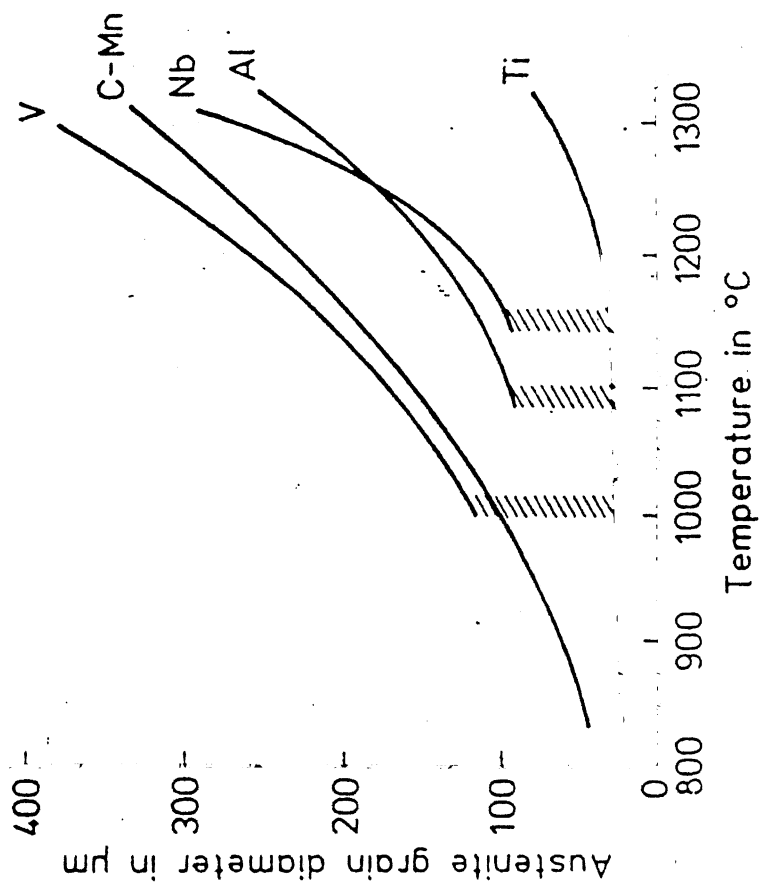
Figure 1.2 : The effect of various microalloying elements on austenite grain growth and the grain coarsening temperature of HSLA steels. [6].
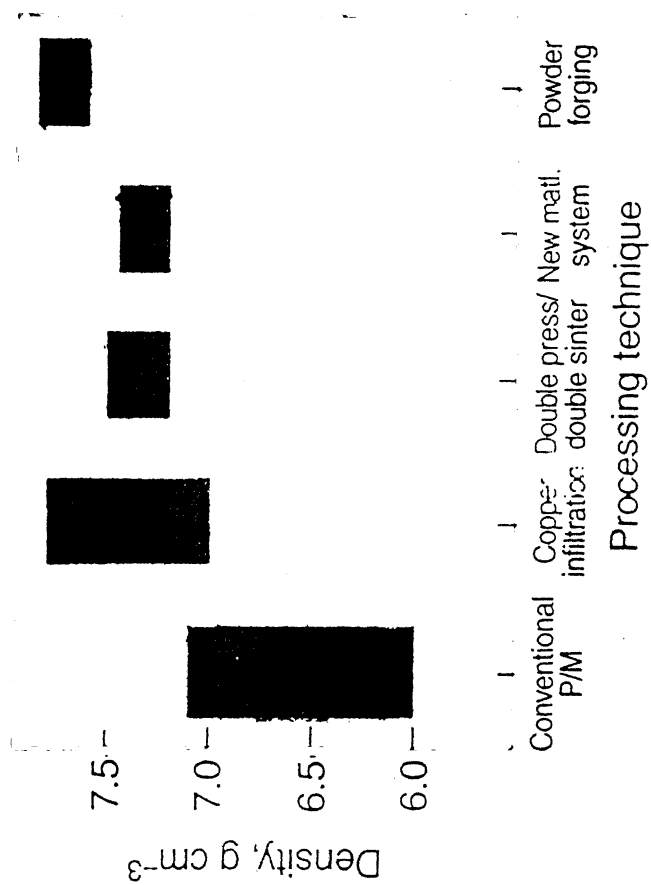
Figure 1.3 : Typical density ranges of ferrous alloys for several common P/M processes. [7].
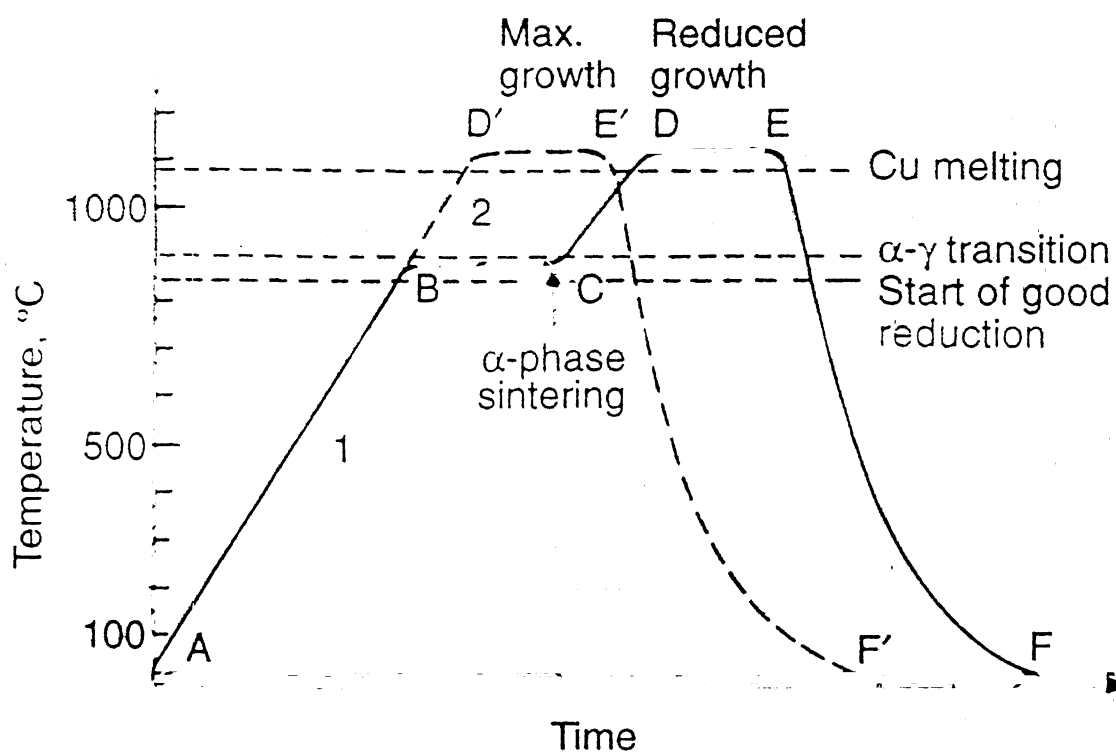
Figure 1.4 : Influence of schematic thermal hysteresis on the copper. [7].

Tensile strength MPa

600

500

400

300

0.5   0.7   0.9

6.8 g cm^{-3}
7.0 g cm^{-3}

2

1

2

1

1–1.5 Cu
2–3 Cu

Elongation, %

6

4

2

0.5   0.7   0.9

1.5 Cu

3 Cu
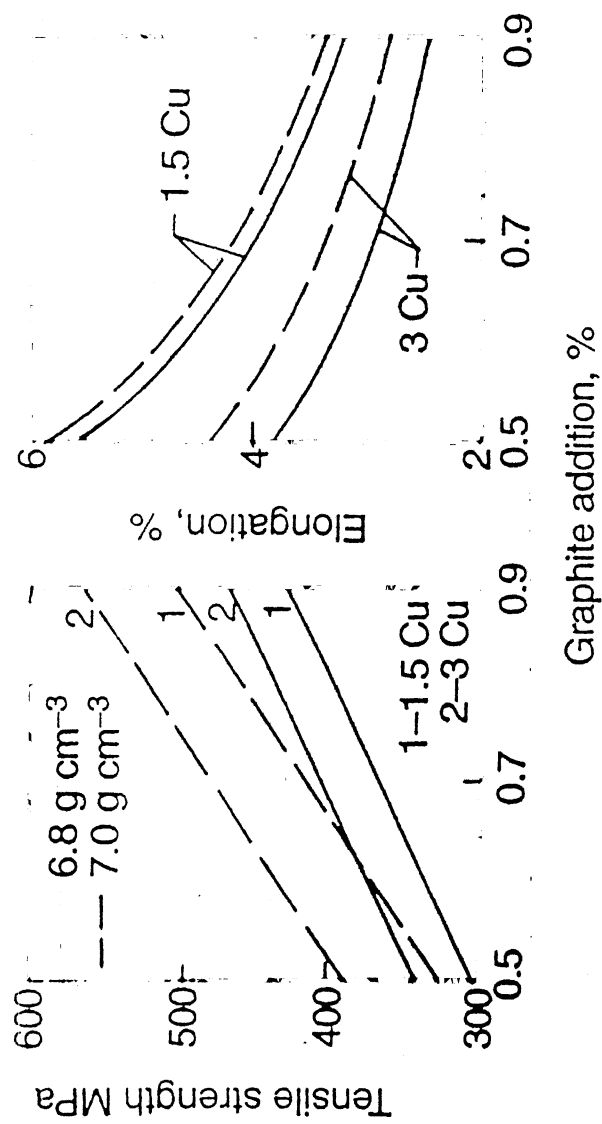
Graphite addition, %

Figure 1.5 : Effect of graphite addition on the tensile strength and elongation of sintered Cu-steels. [7].
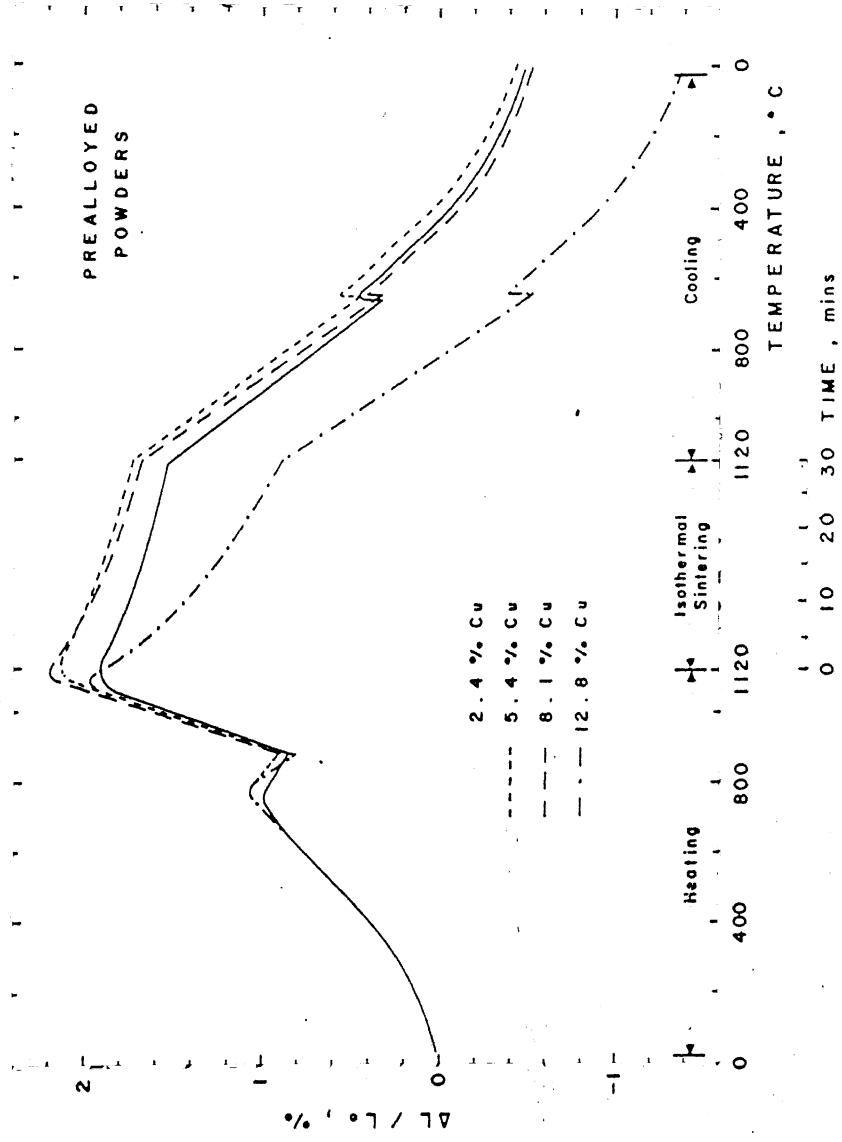
Figure 1.6 : Dilatometric curves corresponding to sintering of compacts of Fe-Cu powders mixed with 1% graphite. [39].
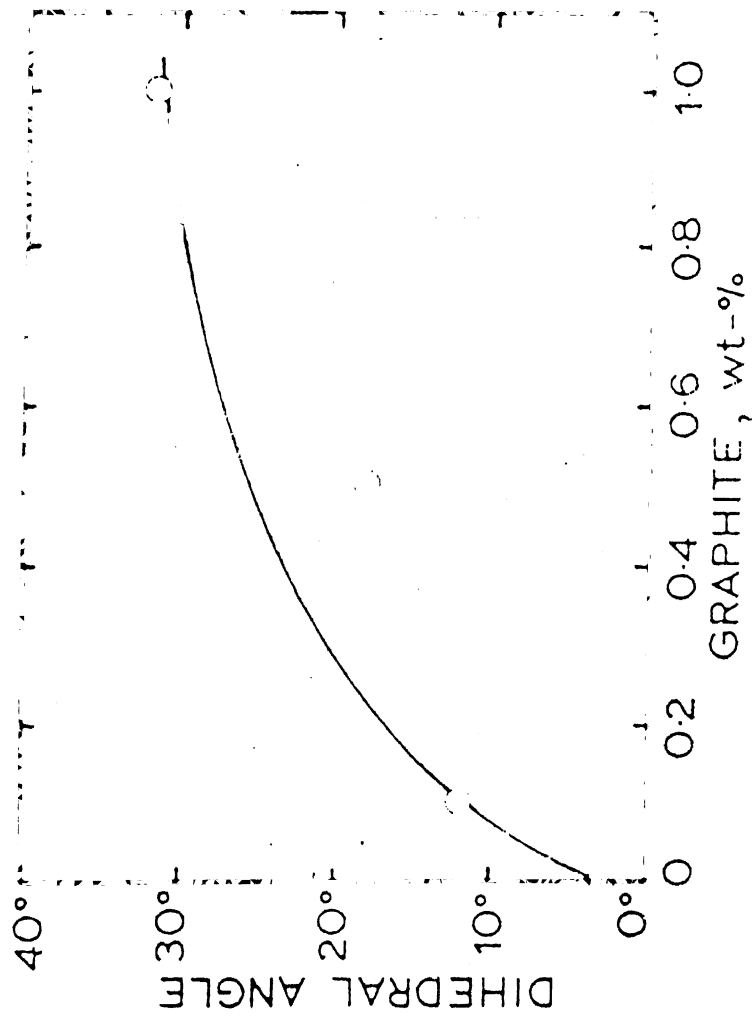
Figure 1.7 : Dihedral angle vs. graphite concentration in ASC 100.29-10Cu sintered at 1140 C for 60 minutes. [24].
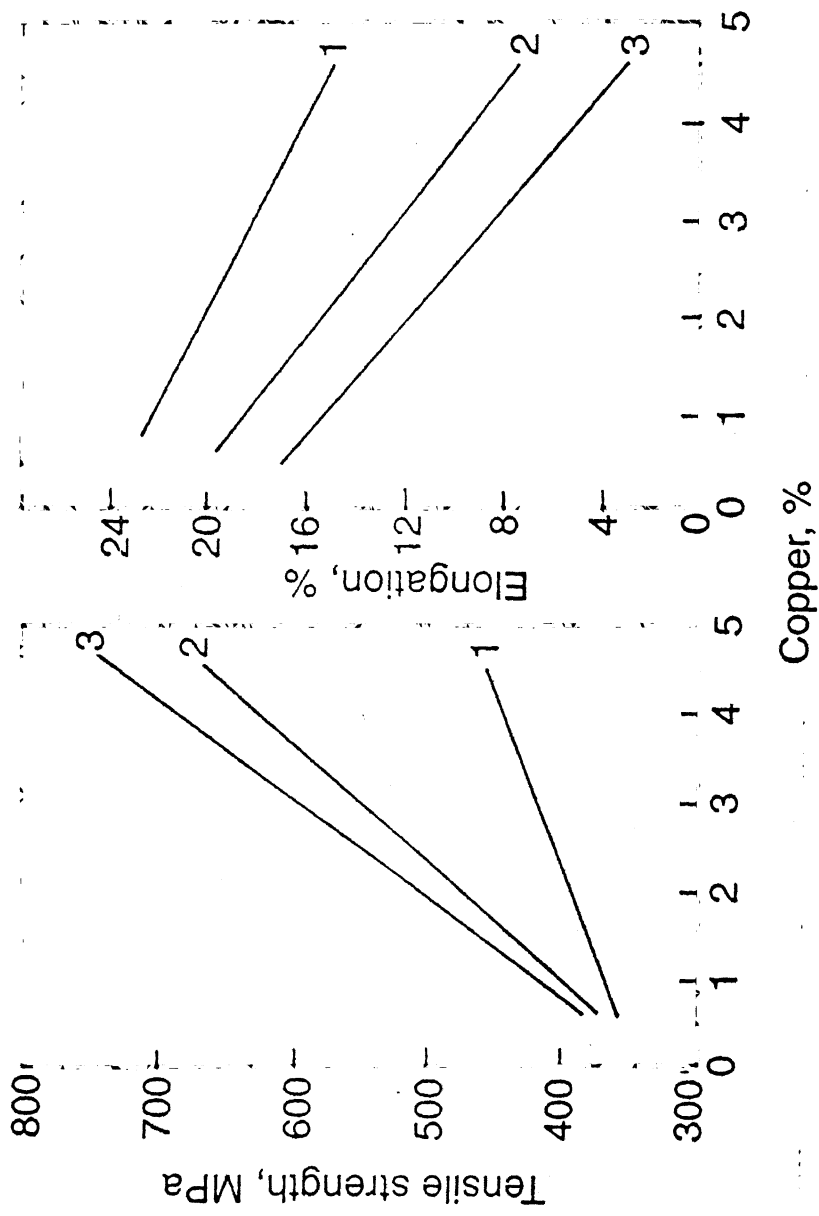
Figure 1.8 : Variation of tensile strength and elongation of various Fe-Cu alloys 1) without Ni, 2) 2.5 Ni, 3) 5Ni. [7].
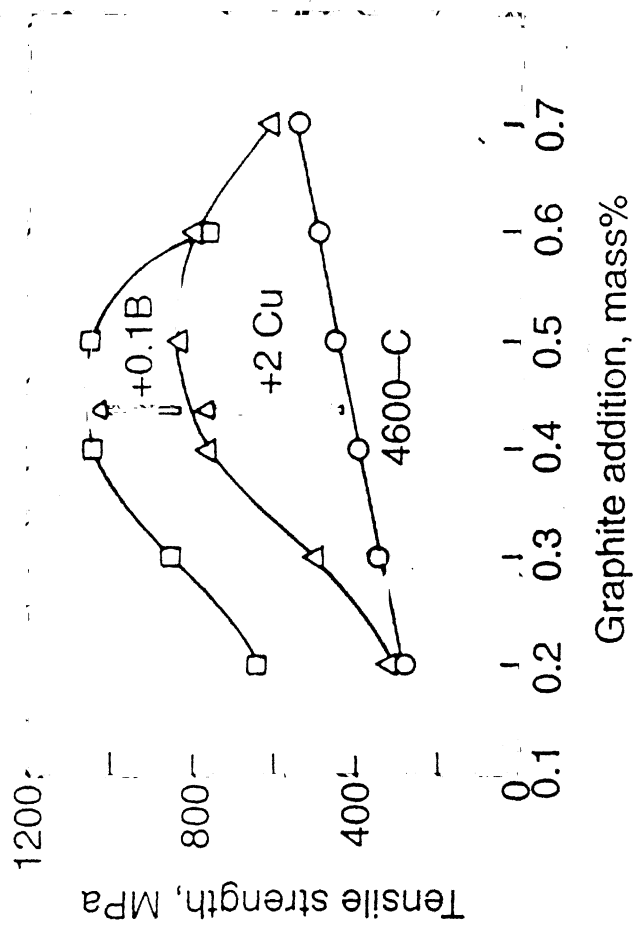
Figure 1.9 : Effect of copper and boron addition on the tensile strength 0f 4600-C system with carbon content. [7].
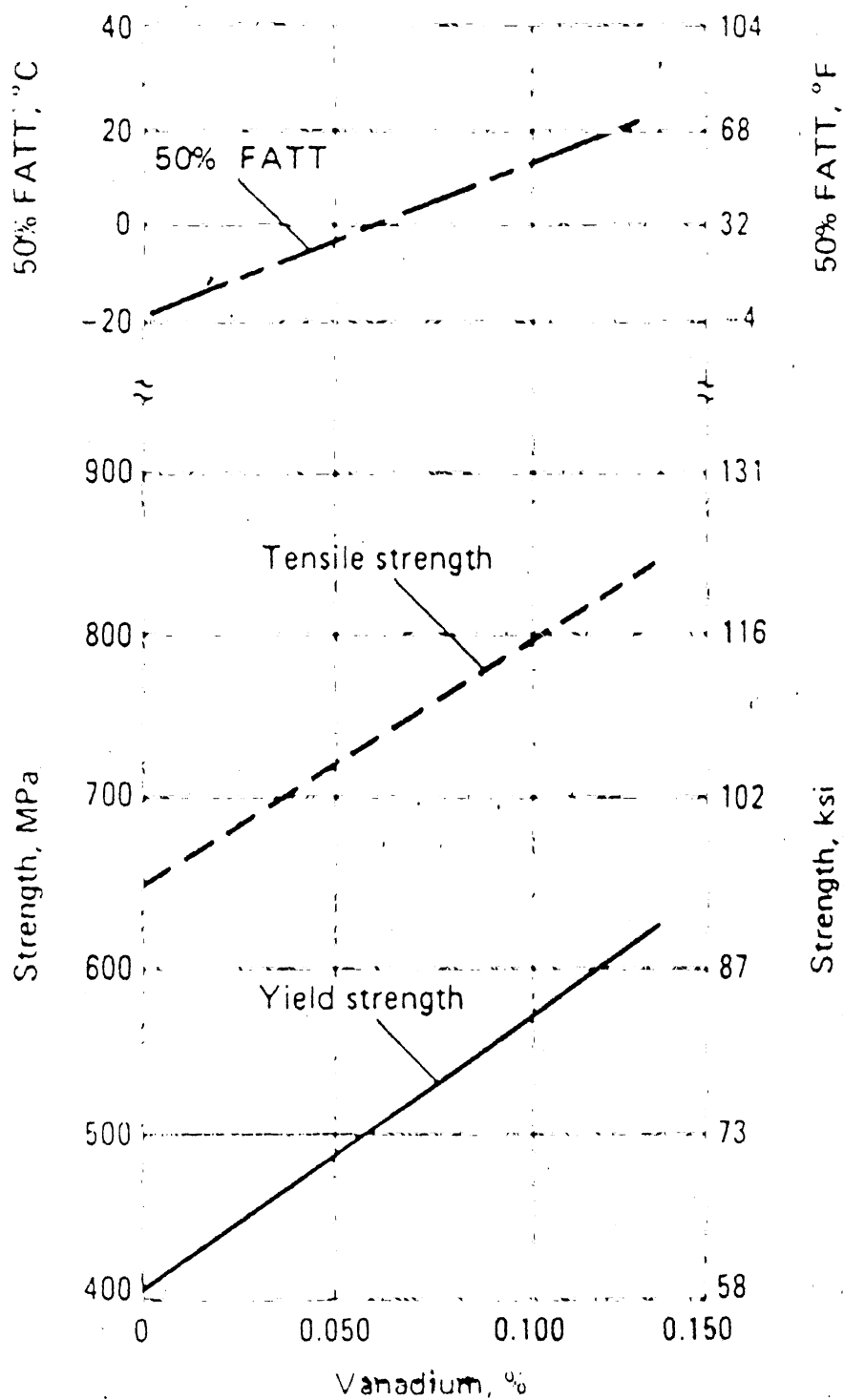
Figure 1.10 : Effect of vanadium on the tensile properties and FATT of a first generation medium carbon microalloy steel. [53].
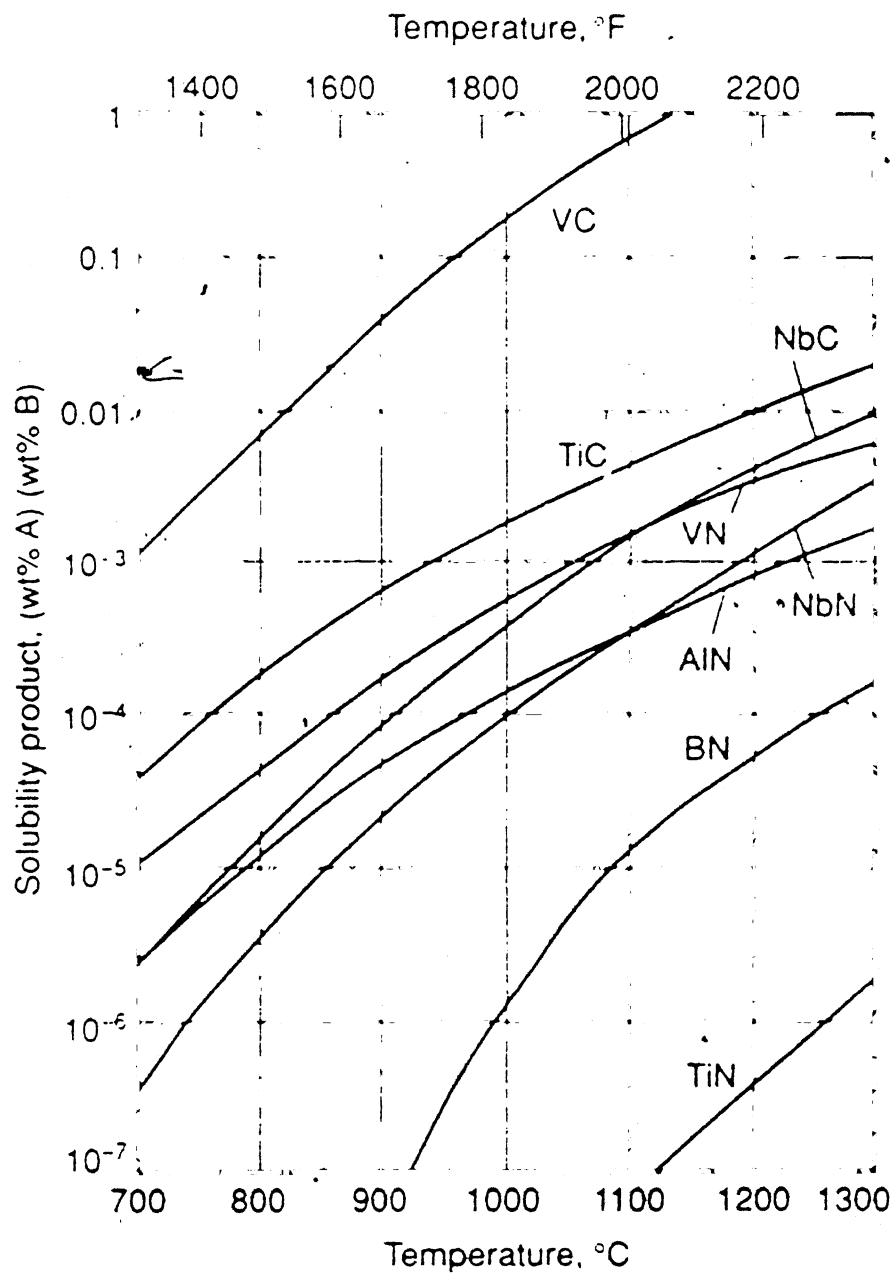
Figure 1.11 : Solubility product versus temperature for carbonitride compounds in austanite. [54].
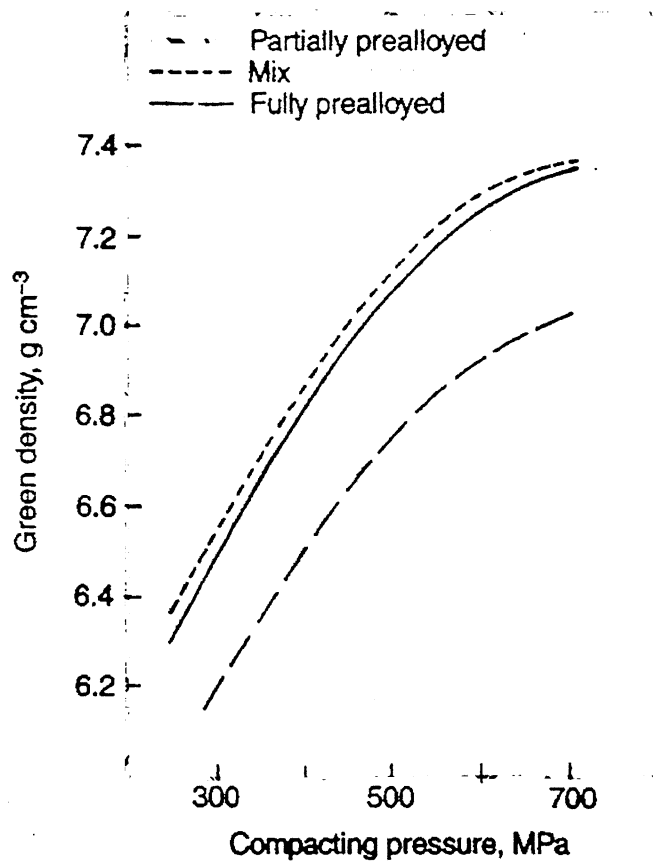
Figure 1.12 : Compressibility curves for powders with 1.75% Ni and 0.5% Mo. [7].

Chapter: 2

Experimental Procedure

The details of experimental procedures followed in the present investigation are described here.

2.1 Powders and Their Characteristics.

The various powders used in this investigation are steel, copper, V(C,N) and graphite powders. The characteristics of these powders are given here.

2.1.1 Low Alloy Steel Powder

The low alloy steel powder used in this investigation was of Astaloy A grade manufacture by Hoganeas Corporation USA. This powder was produced by atomisation. The powder particle size was −325 mesh. The chemical composition of the powder is given below:

Nickel – 1.8%
Manganese – 0.5%
Molybdenum – 0.5%
Iron – Balance.

2.1.2 Copper Powder

The copper powder used in this investigation was supplied by Amrut Industrial Products, Mumbai,India. The powder was produced by electrolytic method and had the size of –400 mesh. The chemical composition of the powder is given below:

Arsenic – 0.002%
Iron – 0.005%
Heavy metals (lead etc.) – 0.008%
Sulphur – 0.005%
Other acid insoluble matter – 0.05%
Copper – balance

2.1.3 Vanadium Carbonitride, VCN powder

The V(C,N) powder used in this investigation was a solid solution of VC and VN. The compound in the form of pellets as supplied by Union Carbide Corporation, New York, USA is called "Nitrovan". The powder was prepared by crushing followed by ball milling of the supplied pellets. The –250 mesh screened powder was used in this investigation. The chemical composition of the powder is given below:

Vanadium – 78.18%
Nitrogen – 11.47%
Carbon – 7.25%
Oxygen – 1.59%
Iron – 0.22%
Chromium – 0.15%
Silicon – 0.02%
Aluminium – 0.01%
Sulphur – 0.009%

Phosphorus – 0.002%

2.1.4 Graphite powder

The graphite powder used in this investigation was natural graphite and was supplied by Ms. Mahindra Sintered Products, Pune.

2.2 Powder Mixture Preparation

The mixtures were prepared with adding different weight fractions of V(C,N), copper and graphite powders to Astaloy A alloy steel powder. The powders were manually blended in mortar and pestle for 30 minutes. The weight fraction of V(C,N) was varied from 0 to 0.6%. The weight percent variation for copper was 0 to 10%. While for carbon i.e., graphite the composition was 0.3% and 0.5% respectively. By varying different components mixtures of fifteen different compositions were prepared.

2.3 Powder Compaction

Powder mixtures of different compositions were cold pressed at room temperature into green compacts in the shape of cylinders. The die used was of conventional type and the resultant green compacts had diameters of 12.76 mm. Hydraulic press was used for the compactions. The compactions were done at a uniform pressure of 625 M Pa. The green pellets thus formed were having green porosity in the range of 18 - 21%. The calculations for green porosity were done using the physical dimensions and mass of the compacts.

2.4 Sintering

All the sinterings were carried out in a silicon carbide resistance heated tube furnace. The alumina tube had a diameter of 4.4cm. and had a constant temperature heating zone of 7 cm. The atmosphere for all the sinterings was flowing hydrogen gas. The purpose of using flowing hydrogen atmosphere was to maintain a reducing atmosphere during sintering. Green compacts were placed in inconel boat, the base of which was coated with alumina powder. The boat was placed in the constant temperature zone. The furnace temperature was controlled within +/- 5 ^{0}C using an analog ON/OFF type controller. The sintering temperature was 1120 ^{0}C. The heating rate of 3-4 ^{0}C per minute was maintained. The holding period at the sintering temperature was kept as 60 minutes in each case. After the sintering was over the compacts were furnace cooled to room temperature, the atmosphere being undeterred.

2.5 Sintered Density Measurement.

Sintered density of compacts was measured using standard water displacement method. [41]. For this the weight of compacts were taken in air and then they were impregnated with xylene using vacuum. They were weighed again, once in air and again in water. Following formula was used to calculate the sintered density [41]:

Density = Wa/(Wxa-Wxw)

Where,

Wa= weight of compact without xylene impregnation in air
Wxa= weight of compact xylene impregnated compact in air
Wxw=weight of compact xylene impregnated compact in water

Using this value, sintered porosity was calculated from the theoretical density value obtained by the rule of mixture.

The changes in physical dimension of the sample were also measured using vernier calipers (Mitutoyo, Japan) having the least count of 0.02 mm.

2.6 Heat treatment.

The sintered compacts were subsequently heat treated in a silicon carbide resistance heated muffle furnace. The atmosphere during the heat treatment was ambient air. The heat treatment temperature was 1000 ^{0}C. The compacts were held for 10 minutes. [34]. To prevent the compacts from getting decarburised, they were wrapped in a special graphite coated foil (sintercast protec tool wrap of stainless steel) before placing them inside the furnace. Compacts were subsequently quenched in a mineral oil at room temperature.

2.7 Microstructural studies.

In metallographic studies, optical microscopy was done. Samples of each composition were studied under optical microscope after sintering as well as after heat treatment. Samples for microscopic studies were prepared in

the conventional manner, starting from belt grinding followed by paper polishing over 80, 320, 600 and 1000 grit size silicon carbide coated papers. This was followed by disc polishing using alumina powder of 0.3 µm size. Polished samples were then etched using $FeCl_3$ solution as etchant. The photographs of the samples were taken on an optical microscope, Metallux 3, Germany make at appropriate magnifications.

2.8 Microhardness.

The Vickers microhardness of all the samples was measured after sintering as well as after the heat treatment. The testing machine was Leitz Microhardness Testing machine, Wetzlar, Germany. A load of 0.100 Kg was applied. At least eight readings were taken on each phase and average value was reported.

2.9 X-ray studies.

X-ray study of various samples were done to study the interactions of alloying addition with the matrix material i.e., Astaloy A. Diffractometer was used to get diffraction peaks of various components in the samples. These peaks were used to recognize the material for further analysis. The instrument used was X-ray powder diffractometer. The models were ISO Debyeflex-1001 (CrKα) and ISO Debyeflex-2002 (CuKα). The instrument was of Rich-Seifert & Co., Germany make.

Chapter: 3

Results

3.1 Densification behaviour

The densification behaviour of steel and its alloy containing copper and VCN in varying amount is shown in figures 3.1-3.3.

In case of copper addition to 0.3%C steel, an increase in sintered porosity is invariably observed with increasing copper content. In case of 0.6% VCN addition, there is a minimum in sintered density for 5% copper addition. In this case sintered density is more for 10% copper addition but still less than the steel where no copper is added (Figure: 3.1). Addition of copper and VCN to 0.3%C steel invariably promotes swelling (Figure: 3.3 and 3.8). The porosity uniformly increases with increase in the copper addition irrespective of VCN content.

In case of 0.5%C steel, addition of VCN promotes compact growth, but this is not uniform with respect to copper addition. For either 0.3% or 0.6% VCN containing steels there is a maximum swelling for 5% copper addition. But in the absence of VCN the maximum growth is for 10% copper addition. The sintered density invariably falls for 0% VCN and increasing copper content (Figure: 3.1 and 3.2). VCN addition results in reduced densification for such steels (Figure: 3.8).

In Fe-Cu-C-VCN system, the maximum densification is observed in the case where neither copper nor VCN is present. The densification is more in the case of 0.5%C steels as compared to 0.3%C steels. The effect of VCN and copper addition to 0.3%C and 0.5% steels do not follow the same trend, the densification in the former case is improved when 10% copper is added along with VCN, which is not observed in the case of 0.3%C steels.

3.2 Microhardness.

The microhardness variations of various phases with varying copper and carbon content in Astaloy-C steels are shown in figures 3.4 - 3.7.

In the case of 0.3%C, steel copper addition invariably increases the microhardness of ferrite and pearlite phases present in the sintered steel (Figure: 3.4 and 3.6). Same trend is followed in oil quenched steels where either ferrite or pearlite or bainite or martensite is observed depending upon the copper content of the steel (Figure 3.5 and 3.7). Heat treatment results in improved microhardness of the steel irrespective of the VCN content. However for 10% copper addition, the microhardness of the steel after heat treatment rises substantially, as much as two times. Increase in VCN content has little effect on the microhardness of any of the phases present in the steel. in fact the microhardness of these phases drops a little with the introduction of VCN. The same trend is followed after the heat treatment. In the case of 0.5%C steel, the

average microhardness variation is similar to that for 0.3%C steel. The effect of heat treatment in hardening becomes more evident with increase in copper content. In the absence of copper there a little difference in the microhardness before and after the heat treatment, but the difference is substantial for 10% copper steel (Figure: 3.5 and 3.7). The effect of VCN is negligible up to 5% copper addition in sintered steel, but the effect is significant in the case of 10% copper addition.

Carbon content variation affects the microhardness of various phases present in the steel to a little extent in as sintered as well as in heat treated conditions.

3.3 Microstructural Studies

The optical microstructures of investigated 0.3%C and 0.5%C steels with or without copper and VCN additions are shown in figures 3.9-3.14. The microstructures of heat treated samples too are shown.

Steels without copper or VCN in as sintered condition exhibit two distinct phases recognized as ferrite and pearlite apart from pores. The microhardness values confirm these observations. The ferrite grains and perlite colonies are relatively large and well dispersed in as sintered condition (Figures: 3.9a and 3.12a). This results in large variations in microhardness values at different

locations. The volume fraction of pearlite is visibly more in 0.5%C steel than in 0.3%C steel.

After heat treatment the microstructural refinement is evident (Figures: 3.9a and 3.12a). Small colonies of pearlite are visible near pores. When VCN is added to the sintered steels, the microstructures show small particles, which are less obvious after heat treatment. This observation is more evident in higher VCN viz. 0.6% VCN content.

After copper is addition the microstructures of as sintered steels are almost similar for both 5% and 10% additions except for the fact that the latter steels contain free copper at the grain boundaries. The two visibly distinct phases in as sintered steels, ferrite and intermixed colonies of pearlite and bainite, are confirmed by their microhardness values (Figures: 3.10,3.11,3.13 and 3.14). The microstructure of heat treated copper steels show martensite, bainite or copper strengthened ferrite depending upon the copper content (Table: 3.1). These phases are confirmed by their microhardness values.

3.4 X-ray Studies

The results of the x-ray study are presented in table 3.2 and 3.3.

From the results it can be inferred that variation of VCN, while keeping copper content constant, results in almost the same 2θ values for iron as well as copper. No other line was observed in any of the compositions.

For the constant VCN, but varying copper content, shifts in the X-ray diffraction line of iron as well as that of copper are observed. The intensities of various characteristic lines too are varying. It is more for iron in 5% copper steels as compared to 10% copper steels.

While copper lines are observed in 10%copper steels no such line is observed in 5% copper steels suggesting complete dissolution of copper in the latter.

From the above observations, it can be inferred that VCN is not much affecting the alloying response of iron and copper in the investigated steels.

Table 3.1: Variuos phases present in sintered and heat treated steels and their average microhardnesses

Composition			Observed phases(Vickers Microhardness)			
			As sintred		After Heat Treatment	
			Phase A	Phase B	Phase A	Phase B
0.3% C	0% VCN	0% Copper	Ferrite(62)	Pearlite(109)	Ferrite(118)	Bainite(158)
		5% Copper	Ferrite(95)	Pearlite(139)	Ferrite(166)	Bainite(158)
		10% Copper	Ferrite(156)	Bainite(183)	-	Martensite(450)
	0.6% VCN	0% Copper	Ferrite(84)	Pearlite(105)	Ferrite(146)	Bainite(158)
		5% Copper	Ferrite(105)	Pearlite(128)	Ferrite(160)	Bainite(158)
		10% Copper	Ferrite(164)	Bainite(193)	-	Martensite(450)
0.5% C	0% VCN	0% Copper	Ferrite(114)	Pearlite(205)	Ferrite(150)	Bainite(158)
		5% Copper	Ferrite(111)	Pearlite(141)	Ferrite(166)	Bainite(158)
		10% Copper	Ferrite(138)	Bainite(198)	-	Martensite(447)
	0.3% VCN	0% Copper	Ferrite(93)	Pearlite(112)	Ferrite(112)	Bainite(158)
		5% Copper	Ferrite(119)	Pearlite(138)	Ferrite(200)	Bainite(158)
		10% Copper	Ferrite(187)	Bainite(228)	-	Martensite(420)
	0.6% VCN	0% Copper	Ferrite(95)	Pearlite(110)	Ferrite(125)	Bainite(158)
		5% Copper	Ferrite(96)	Pearlite(128)	Ferrite(185)	Bainite(158)
		10% Copper	Ferrite(192)	Bainite(350)	-	Martensite(450)

Table 3.2: X-ray(CuKα) data for steels with constant copper but varying VCN content.

Iron

(hkl)	in 0.0% VCN steel		in 0.3% VCN steel		in 0.6% VCN steel	
	2θ (Degrees)	Lattice parameter,A°	2θ (Degrees)	Lattice parameter,A°	2θ (Degrees)	Lattice parameter,A°
110	44.60	2.8708	44.60	2.8708	44.70	2.8646
200	65.00	2.8711	65.00	2.8672	65.10	2.8634
211	82.15	2.8716	82.25	2.8687	82.35	2.8660
220	98.65	2.8727	98.70	2.8716	98.95	2.8662
310	115.95	2.8731	116.30	2.8676	116.20	2.8692
222	N.A.	-	136.65	2.8713	136.75	2.8704
Lattice parameter following extrapolation method [57]	2.8746		2.8730		2.8718	
% shift with respect to 0% VCN steel	-		-0.0557		-0.0974	

Copper

(hkl)	0% VCN steel		0.3% VCN steel		0.6% VCN steel	
	2θ (Degrees)	Lattice parameter,A°	2θ (Degrees)	Lattice parameter,A°	2θ (Degrees)	Lattice parameter,A°
111	43.350	3.6123	43.30	3.6163	43.30	3.6163
200	50.500	3.5115	N.A.	-	50.50	3.6115
Lattice parameter following extrapolation method [57]	3.6121		-		3.6105	
% shift with respect to 0% VCN steel	-		-		-0.0443	

%Shift = (Final lattice parameter- Initial lattice parameter)X100/ Initial lattice parameter

Table 3.3: X-ray(CrKα) data for steels with constant VCN but varying copper content.

Iron

(hkl)	0 %Cu steel		5% Cu steel		10% Cu steel	
	2θ (Degrees)	Lattice parameter, A°	2θ (Degrees)	lattice parameter	2θ (Degrees)	Lattice parameter, A°
110	68.80	2.8658	68.70	2.8694	68.65	2.8712
200	106.10	2.8651	105.80	2.8704	105.65	2.8737
Lattice parameter following extrapolation method [57]	2.8643		2.8716		2.8762	
% shift with respect to 0% VCN steel	-		0.25		0.42	

Copper

(hkl)	standard state		10% Cu steel	
	2θ (Degrees)	Lattice parameter, A°	2θ (Degrees)	Lattice parameter, A°
111	66.50	3.6165	67.00	3.5923
200	78.58	3.6160	79.00	3.5997
220	127.23	3.6147	127.40	3.6120
Lattice parameter following extrapolation method [57]	3.6150		3.6138	
% shift with respect to 0% VCN steel	-		-0.03	

%Shift = (Final lattice parameter- Initial lattice parameter)X100/ Initial lattice parameter
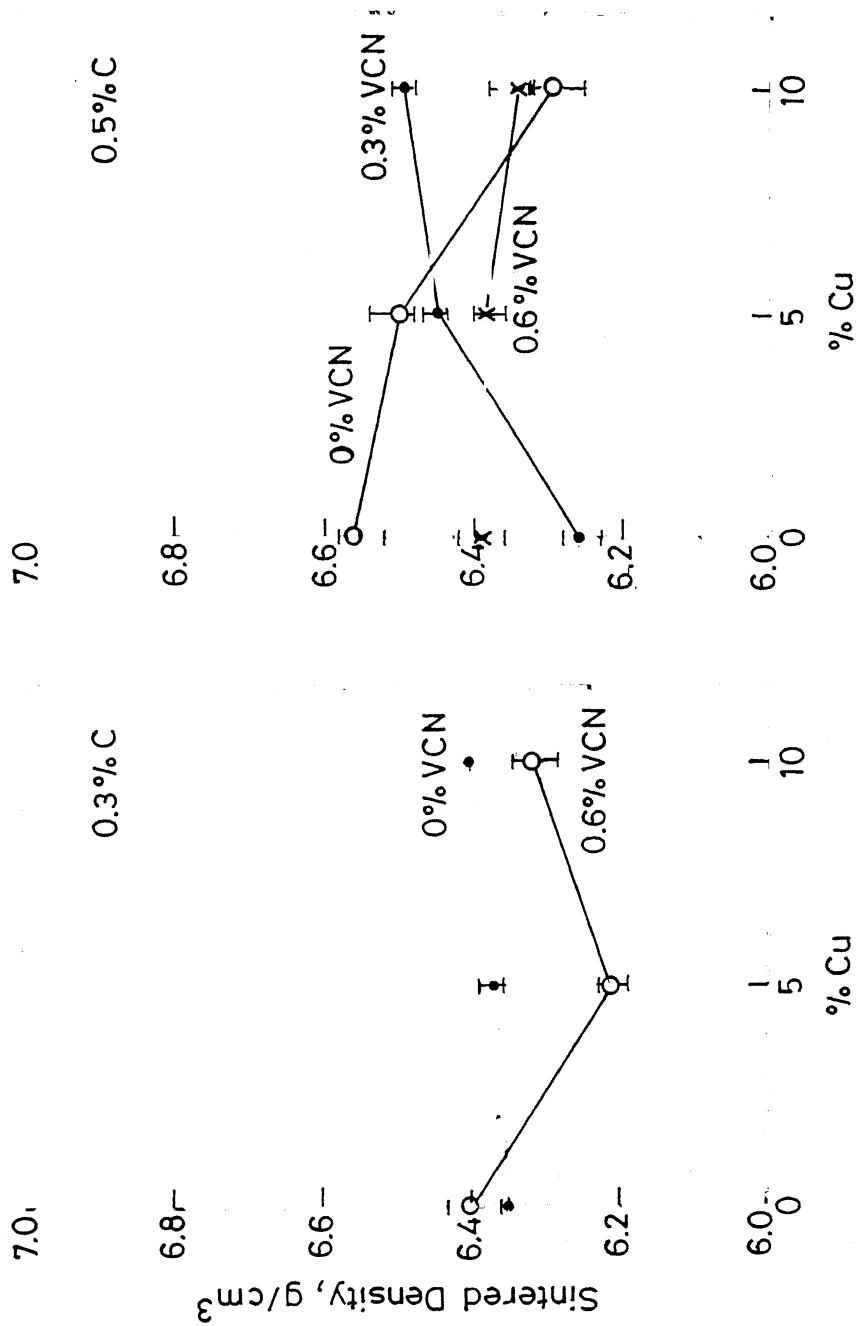
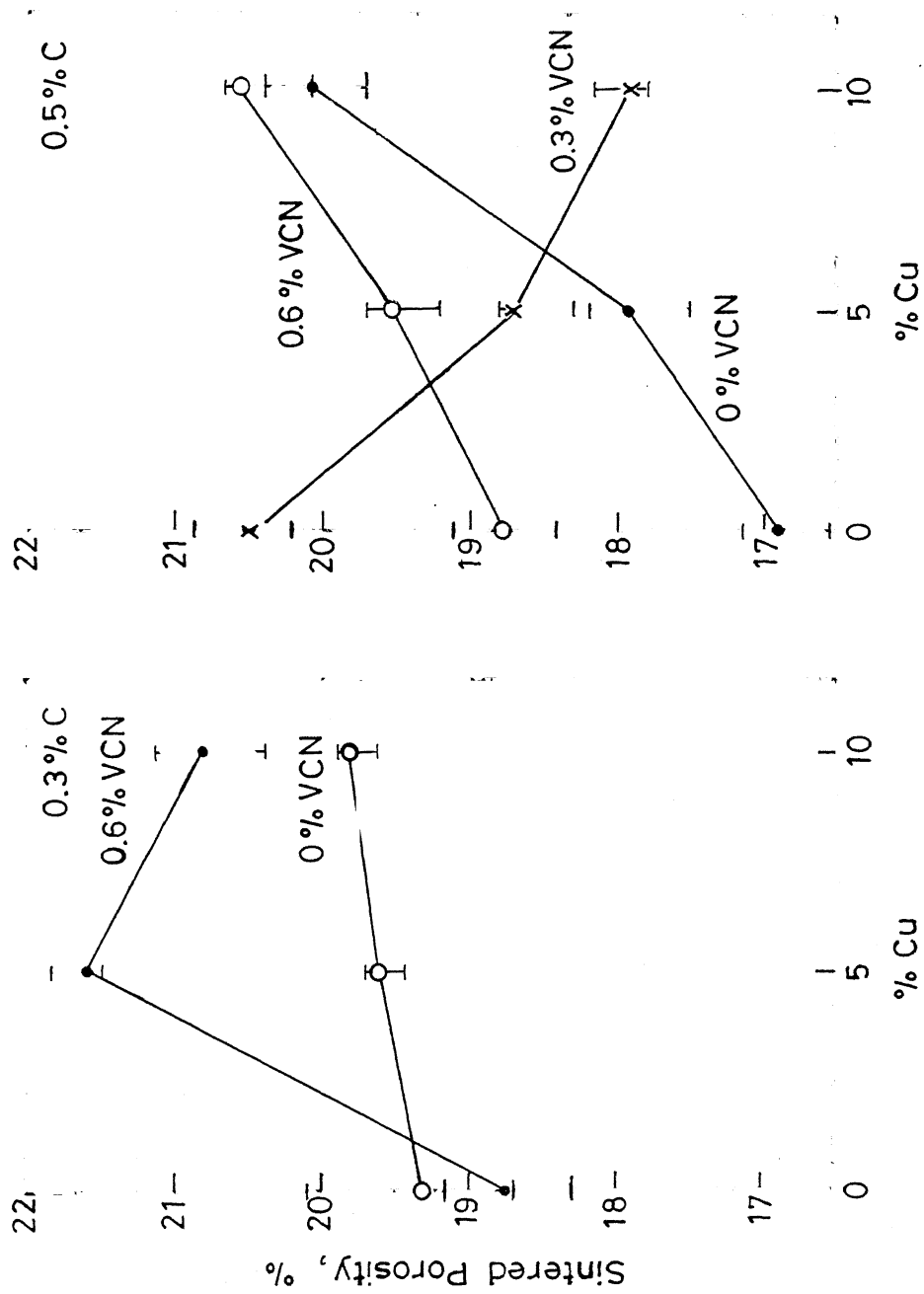Figure 3.1: Variation of sintered density with respect to copper content in steel.

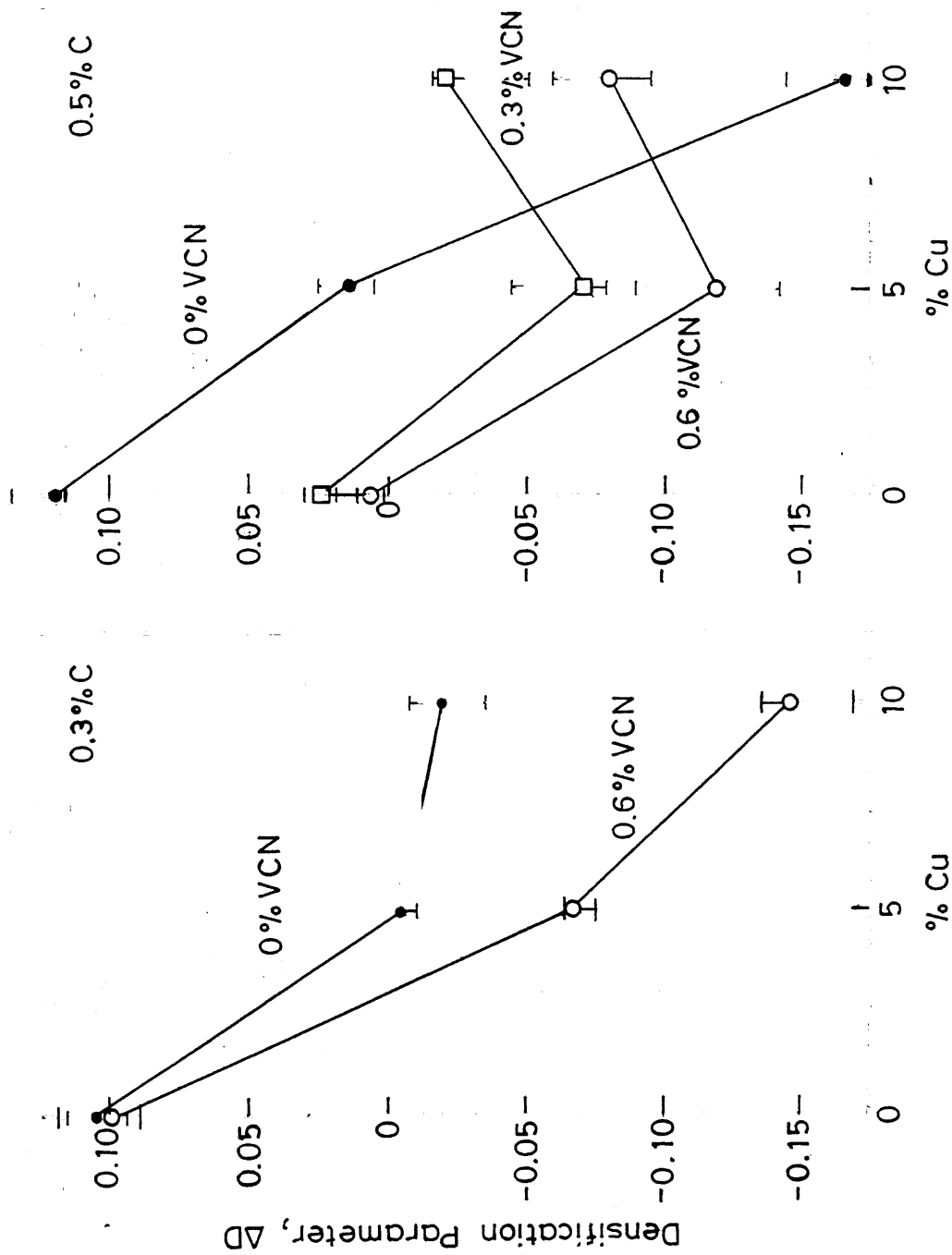Figure 3.2: Variation of sintered porosity with respect to copper content in steel.

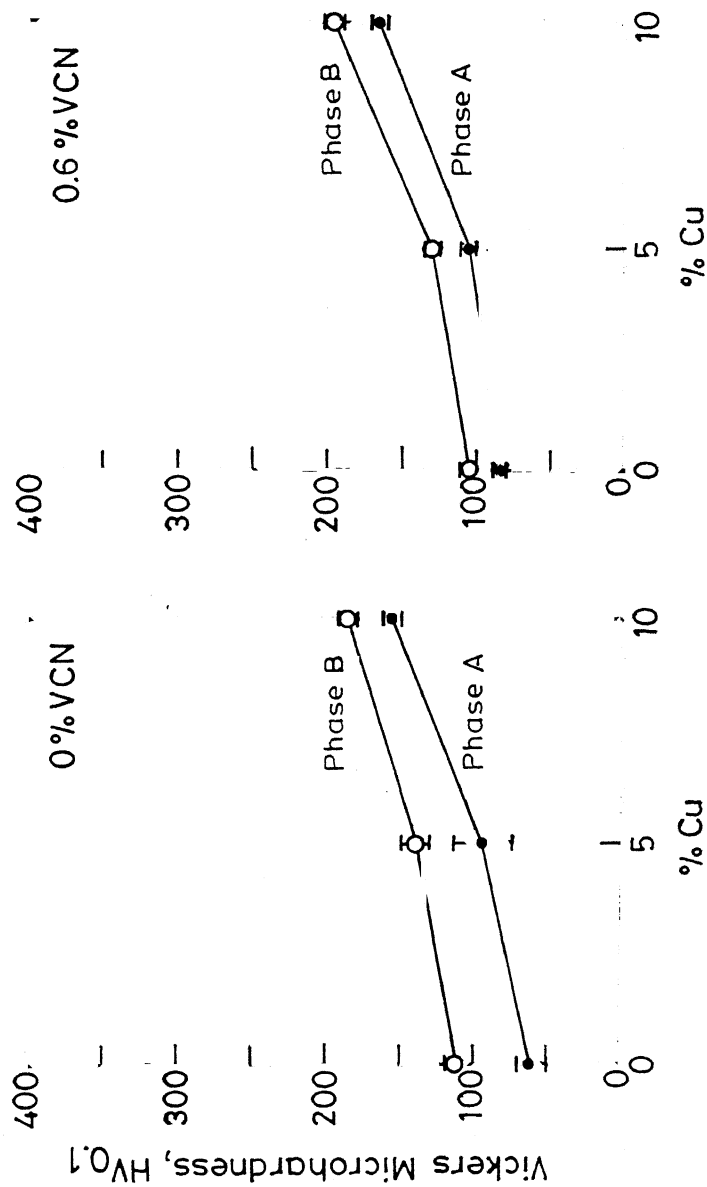Figure 3.3: Variation of densification parameter with respect to copper content in steel.

Figure 3.4: Variation of microhardnesses of various phases in as sintered 0.3%C steel with respect to copper content.
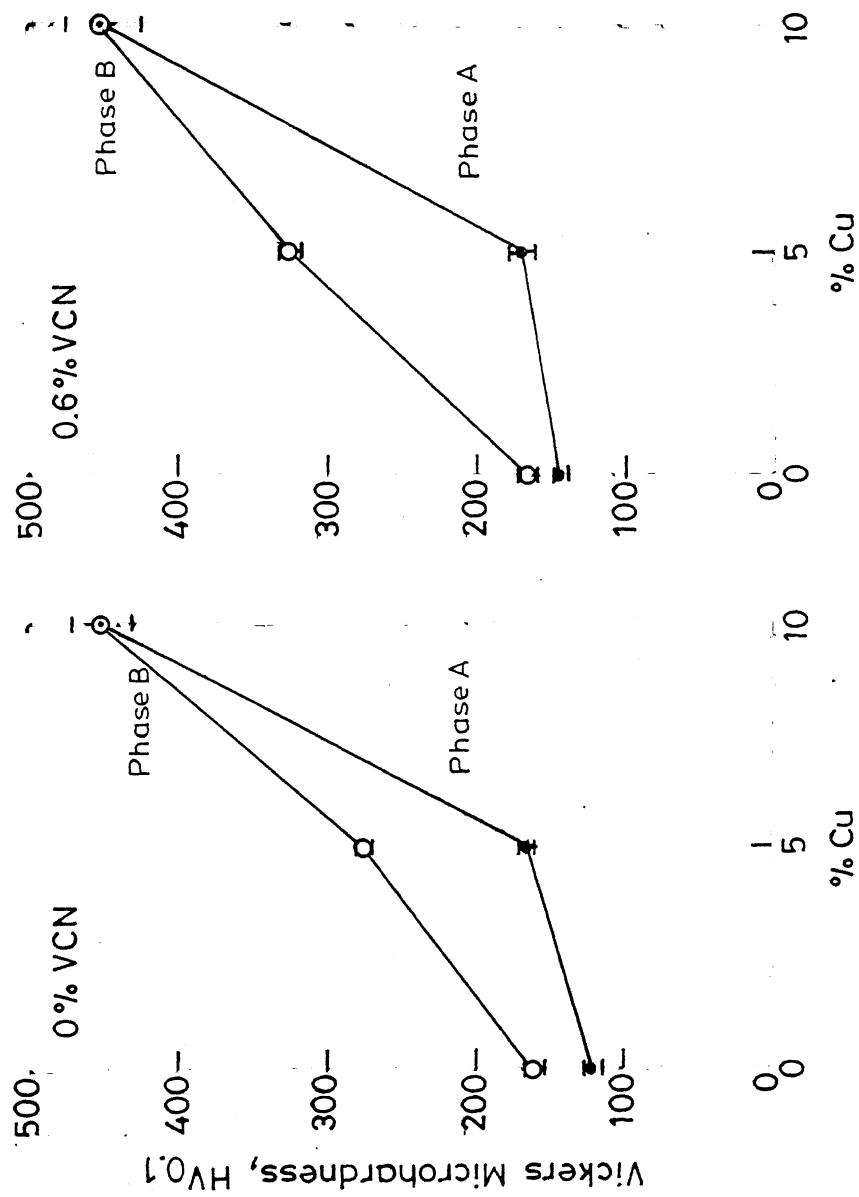
Figure 3.5: Variation of microhardnesses of various phases in oil quenched 0.3%C steel with respect to copper content.
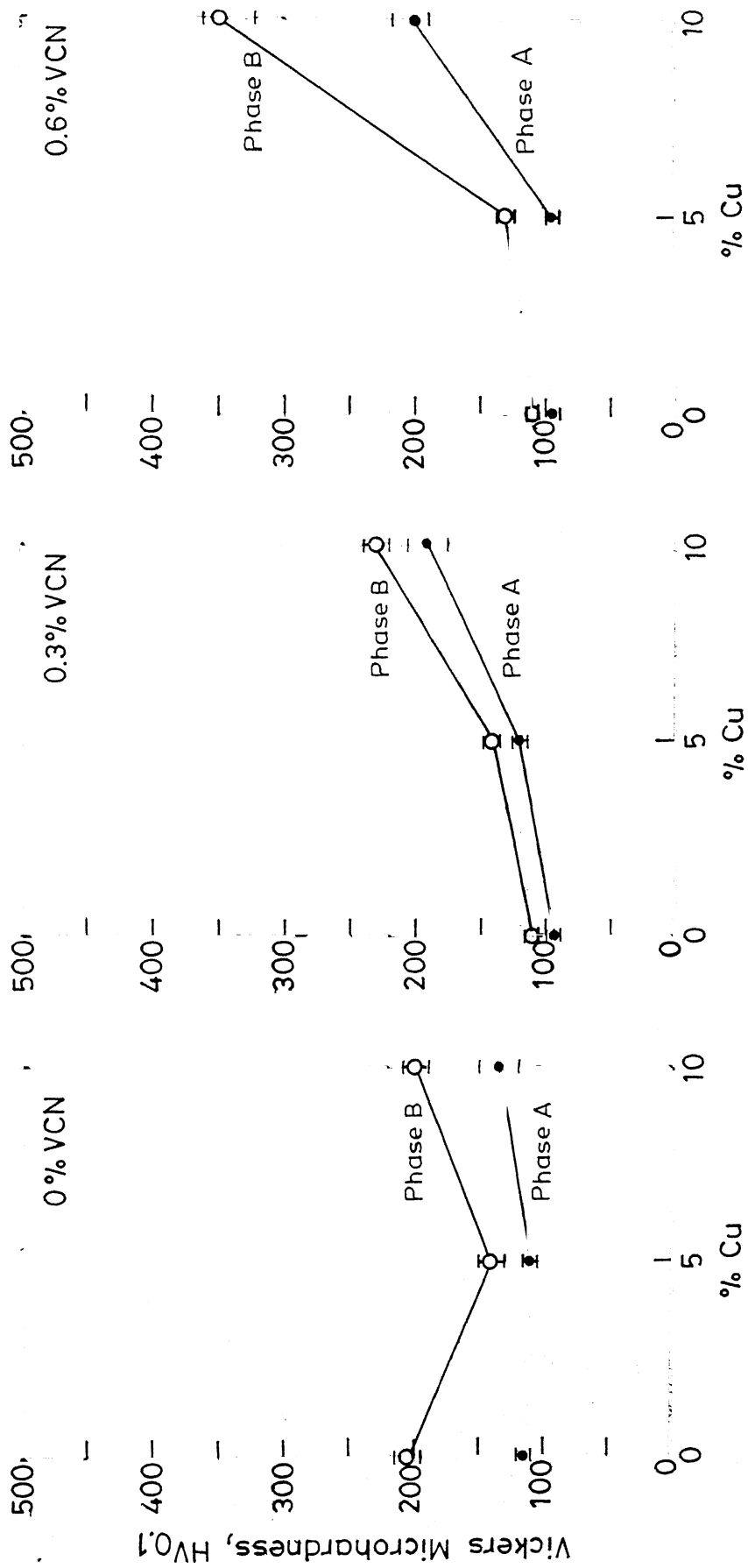
Figure 3.6: Variation of microhardnesses of various phases in as sintered 0.5%C steel with respect to copper content.
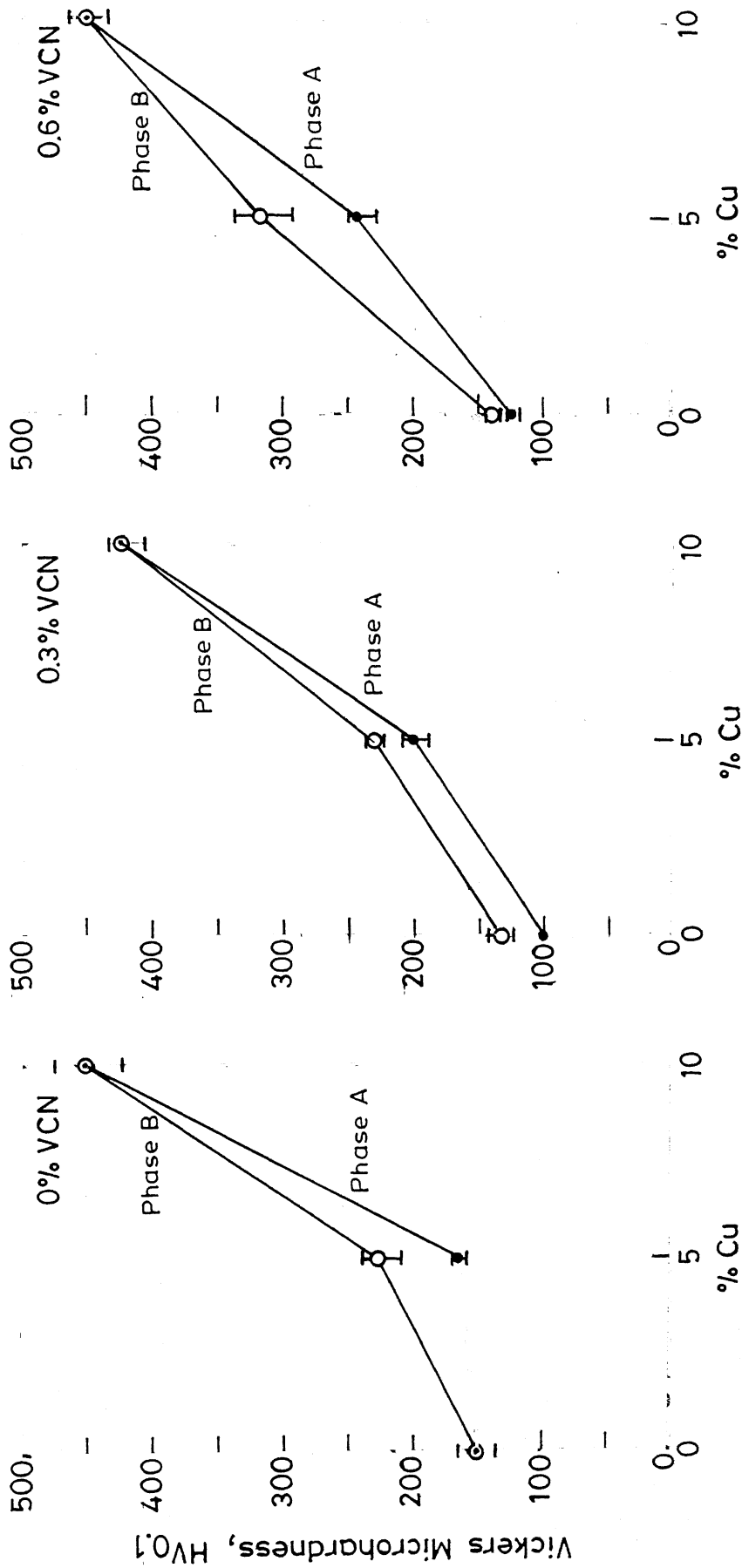
Figure 3.7: Variation of microhardnesses of various phases in oil quenched 0.5%C steel with respect to copper content.
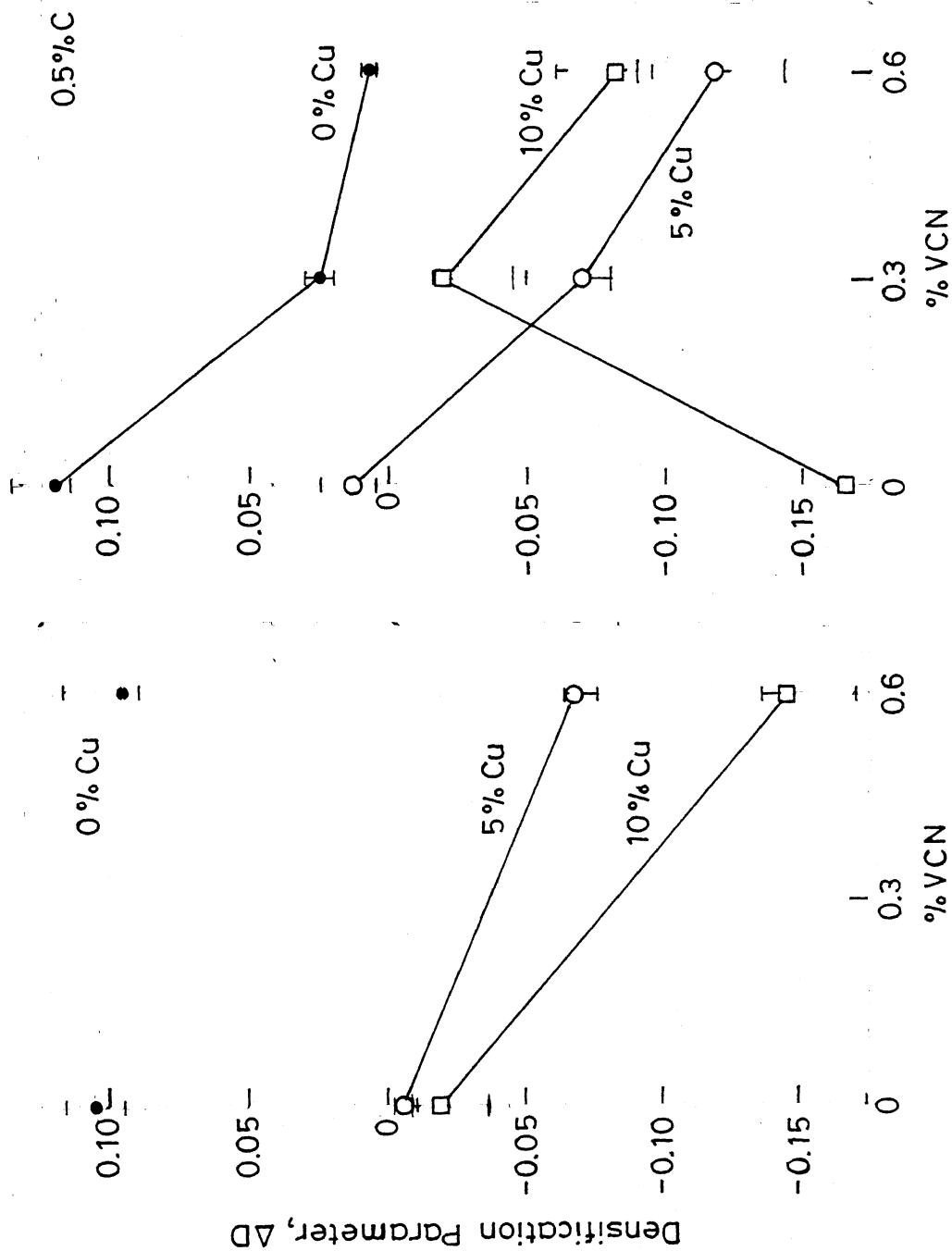
Figure 3.8: Variation of densification parameter with respect to VCN content in steel.
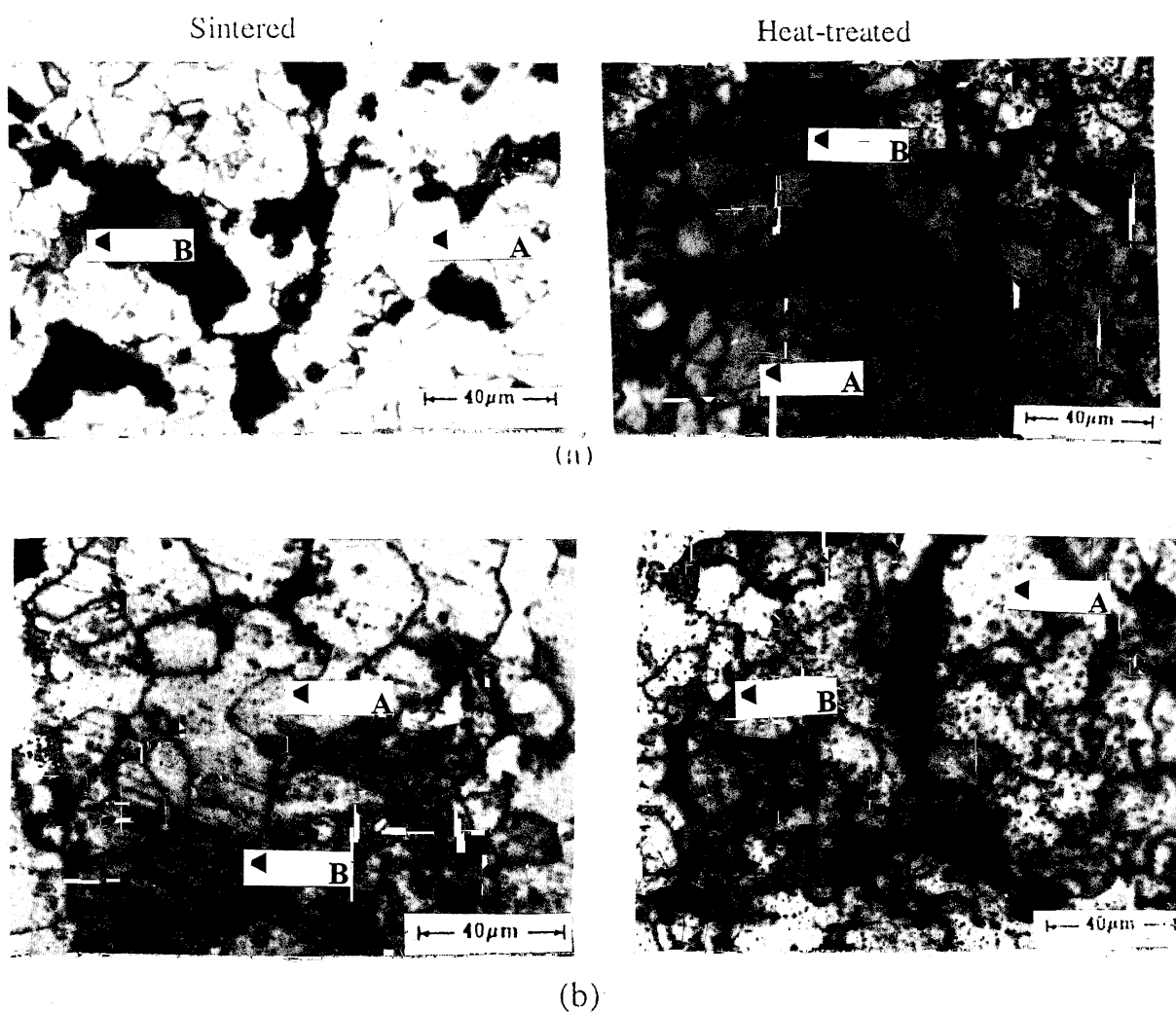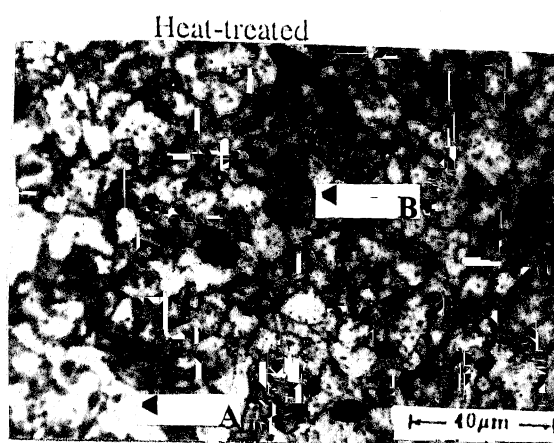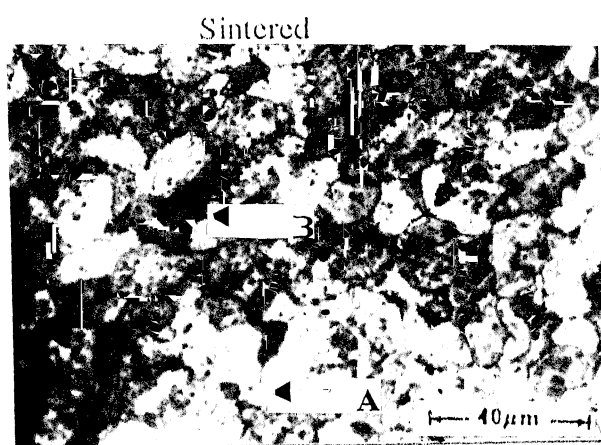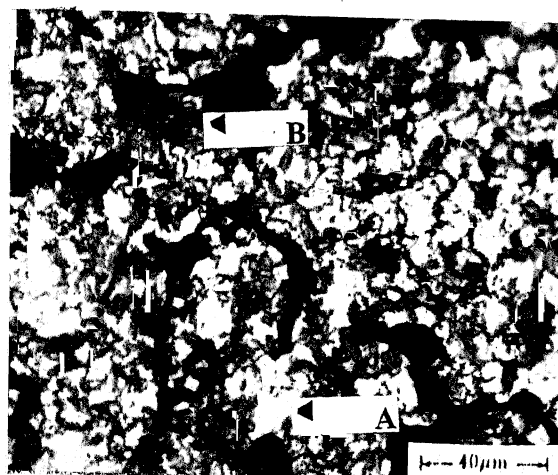
Sintered   Heat-treated

(a)

(b)

Fig. 3.9 Microstructures of sintered and heat-treated 0.3% C – 0% Cu steel
(a) 0%VCN (b) 0.6% VCN

For details of phases A and B see Table 3.1

Sintered Heat-treated

(a)

(b)

Fig. 4.10 Microstructures of sintered and heat-treated 0.3% C – 5% Cu steel
(a) 0% VCN (b) 0.6% VCN

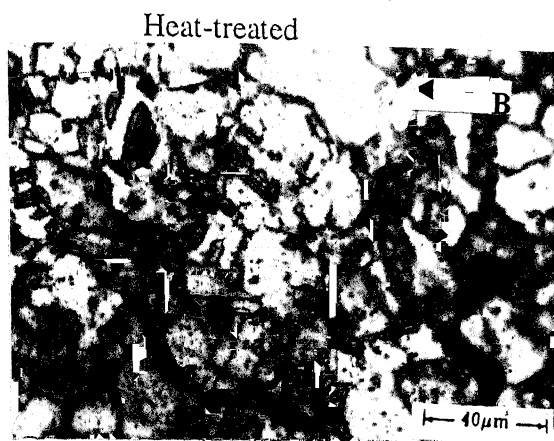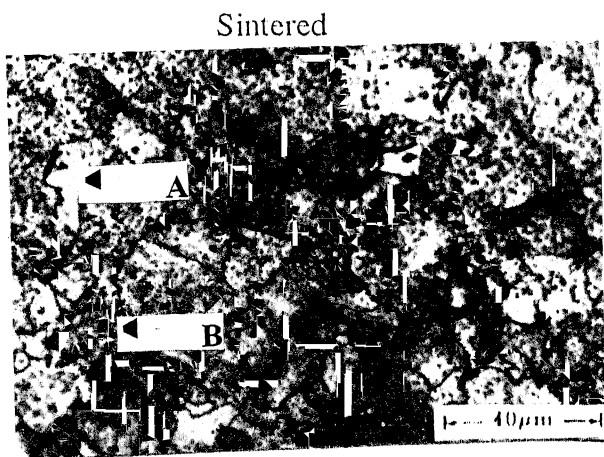**For details of phases A and B see Table 3.1**

Sintered   Heat-treated

(a)

(b)

Fig. 3.11 Microstructures of sintered and heat-treated 0.3% C – 10% Cu steel
(a) 0% VCN (b) 0.6% VCN

For details of phases A and B see Table 3.1
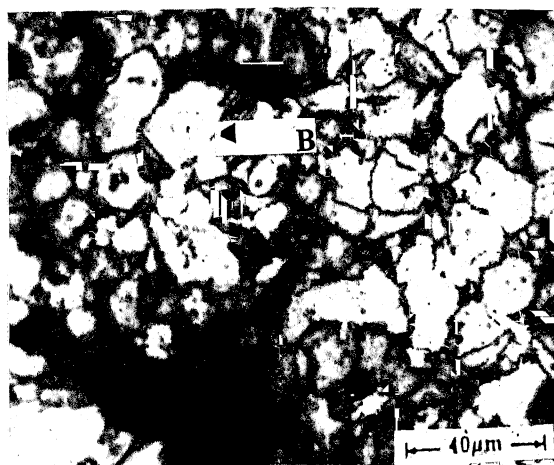
Sintered   Heat- treated

(a)

(b)

(c)

Fig. 3.12 Microstructures of sintered and heat-treated 0.5% C – 0% Cu steel
(a) 0%VCN (b) 0.3% VCN (c) 0.6% VCN
For details of phases A and B see Table 3.1

Sintered   Heat-treated

(a)

(b)
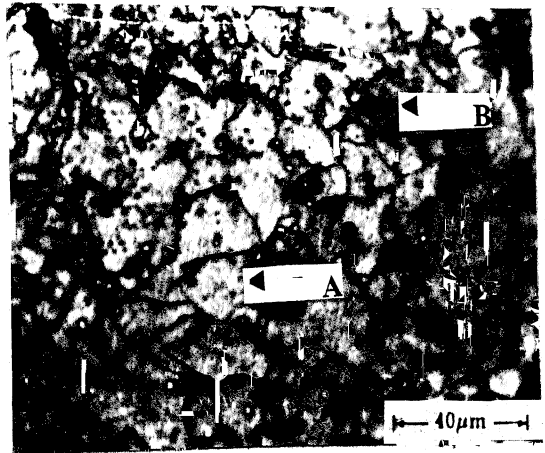
(c)
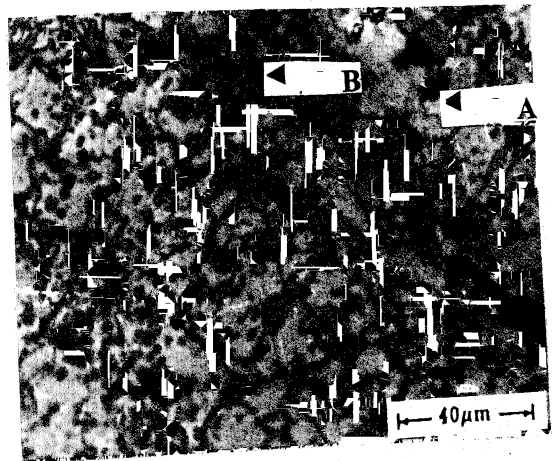
Fig. 3.13 Microstructures of sintered and heat-treated 0.5% C – 5% Cu steel
(c) 0%VCN (b) 0.3% VCN (c) 0.6% VCN

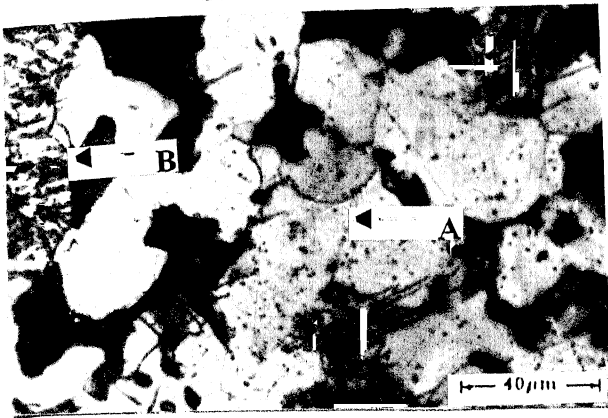**For details of phases A and B see Table 3.1**
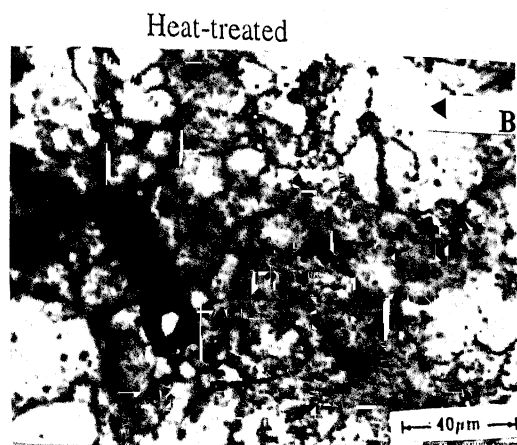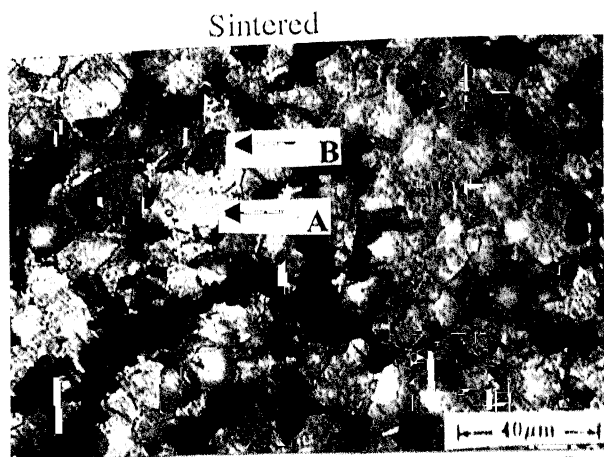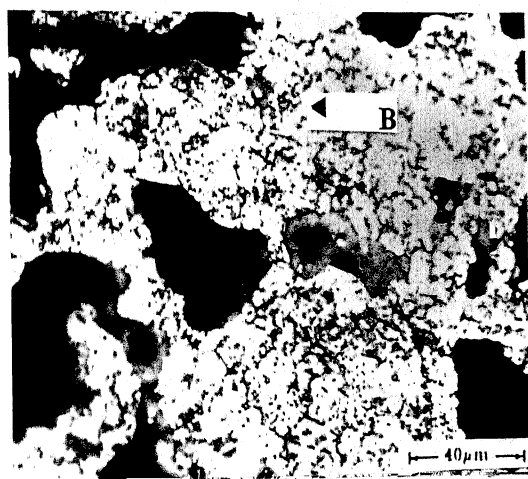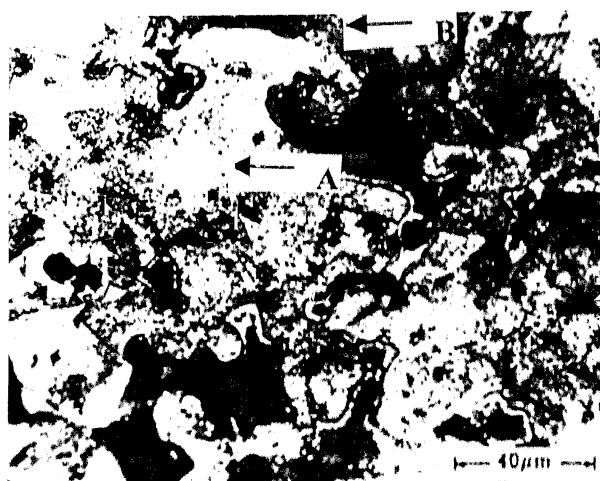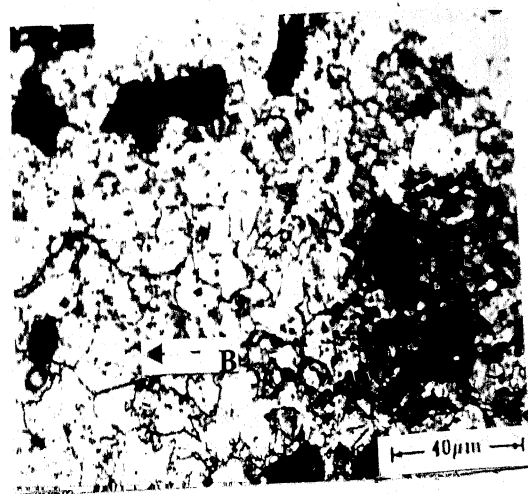
Fig. 3.14 Microstructures of sintered and heat-treated 0.5% C – 10% Cu steel
(b) 0%VCN (b) 0.3% VCN (c) 0.6% VCN

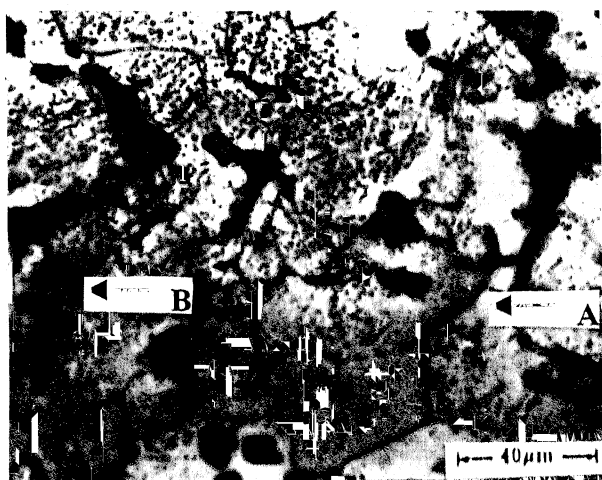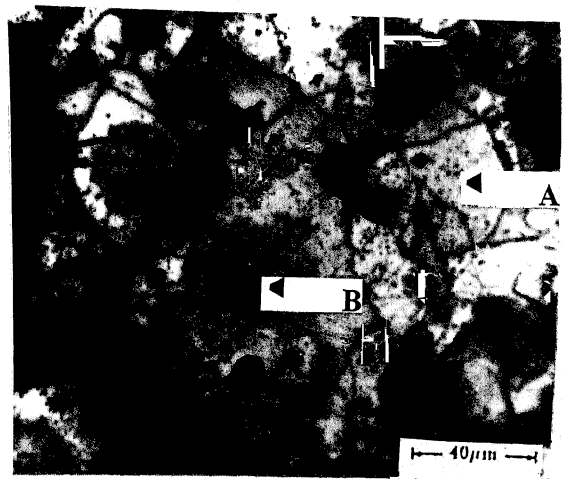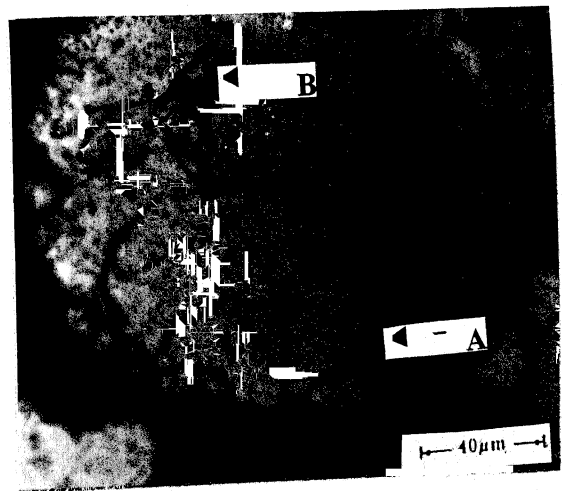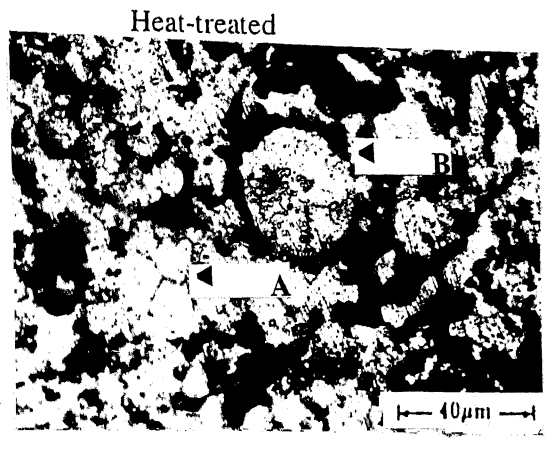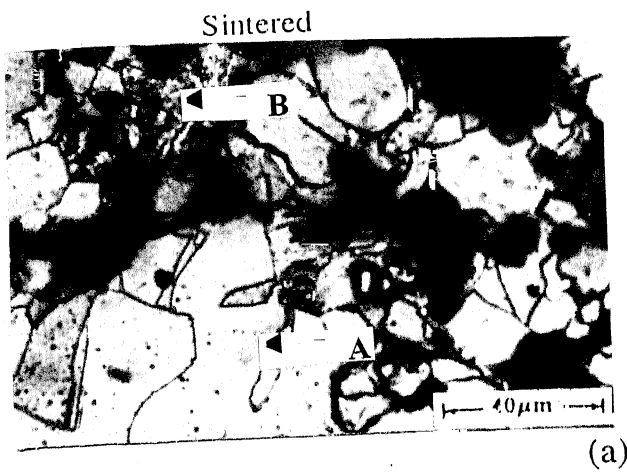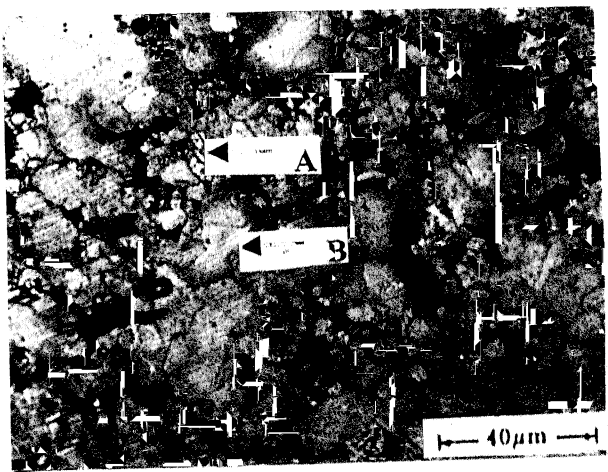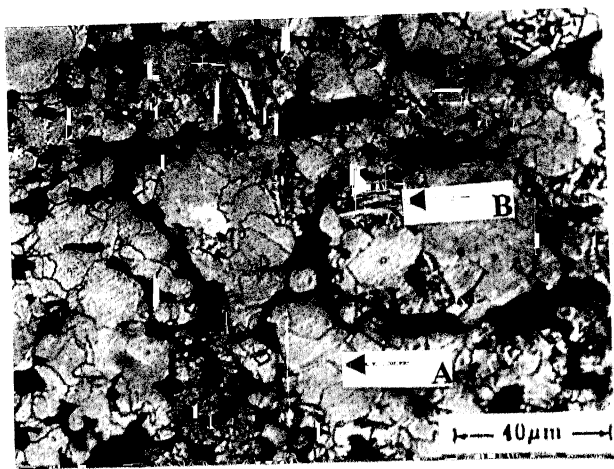**For details of phases A and B see Table 3.1**

Chapter: 4

Discussion

4.1 Role of Copper

Copper when added to plain carbon steels is expected to compensate for shrinkage during sintering caused by carbon in iron. The usual amount for zero dimensional changes is about 2%. But when more copper is added expansion is observed. [7,11,23,24]. The present results confirm this fact (figure 3.1-3.3). The extent of expansion in the investigated steel increases with increasing copper content from 5% to 10%. X-ray studies of sintered steels show no copper line for 5% copper addition but they are present in the case of 10% copper steel (figure 4.1 and 4.2). This suggests that in 5% copper steel all copper is dissolved, while some undissolved copper is present in 10% copper steel. Further, the results (Table 3.2) show that with increasing copper content in the steel the lattice parameter of iron expands substantially, but negligible effect is observed on copper lattice parameter. Negligible change in lattice parameter of copper in the steel as compared to that of pure standard copper confirms no dissolution of iron in copper. It can be inferred that dissolution of copper into iron lattice causes the expansion in the lattice parameter, which increases with increasing copper

content. It is this lattice expansion which is responsible for compact growth during sintering. This observation is in line with the previous work. [21].

The presence of copper lines in case of 10% copper steels but not in 5% copper steels suggests a limit of copper solubility in iron between 5% and 10% copper addition. This observation is again in confirmation with earlier works. [15,18,19].

Copper addition in the presently investigated sintered steels results in increased microhardness of various phases present (Figure: 3.4-3.7). This suggests that even if compacts have grown during sintering, copper addition has positive hardening effect. Increase in hardness of sintered steel with increasing copper is due to solid solution strengthening effect apart from enhanced liquid phase sintering for high copper containing steels.

Copper addition in Ni-Mo-Mn sintered steels increases its hardenability particularly if nickel concentration is limited to 2%. [42,46]. Since the composition of steel powder used in this investigation conforms to the above, it is possible that substantial increase in the hardness for 10% copper addition is due to increased hardenability during heat treatment. Copper is expected to impart hardenability till it goes into the solution with steel. 5% copper completely dissolves in steel suggesting all the copper is used for hardening. Even if some copper remains undissolved in 10% copper steel, it can be said that

more than 5% copper is available for hardening in this steel and hence better hardenability of this steel is expected. The cooling rate during oil quenching is generally 9 ^{0}C, while in furnace cooling it is 0.2 ^{0}C. [55]. A possible CCT diagram and phase constituents diagram is given in figure 4.3. It shows that substantial amount of martensite is present in steel after oil quenching even if the copper content of the steel in above case is only 1.5%. Since copper increases hardenability, a further increase in martensite volume fraction and its associated effect as hardness is expected.

Copper addition affects the microstructure of sintered as well as heat treated steels. Since solubility of copper in iron is less than 10% undissolved copper pools appear in the microstructures of steels containing 10% copper. These pools are mostly located at grain boundaries, which is expected due to presence of carbon. Bigger sized pools are evident in case of 0.5% C steels as more carbon results in larger dihedral angle resulting in further reduction in copper penetration in between iron grains. [23,24,39]. Substantial amount of pearlite is observed in 5% copper sintered steels, while the microstructure of 10% copper sintered steel is dominated by bainite. The absence of pearlite and the presence of low amount of bainite in the microstructures of 10% copper heat treated steels confirm that martensite forms at the cost of these phases (Figure: 3.11 and 3.14).

4.2 Role of vanadium carbonitride, VCN

VCN is a refractory hard phase. When it is added to steel it is not expected to aid densification of steel during sintering, 'such a behaviour is confirmed in this investigation. The more is the amount of VCN in the steel the less is the densification (Figure: 3.8). The X-ray studies done to examine the role of VCN during sintering of steels show that VCN particles do not get dissolved during sintering. This is evident from the fact that with an increase VCN content, there is no measurable shift in the position of iron or copper X-ray diffraction lines. The fact that more amount of VCN decelerates densification is confirmed by microhardness measurement (Table: 3.1).

However when VCN is added to copper bearing 0.5%C steels, the maximum swelling is observed in case of 5% copper addition. In case of 10% copper steel, the presence of VCN impedes copper growth because of better sinterability at higher volume fraction of copper melt. The same trend is not observed in 0.3%C steels. The decreasing slope of ΔD versus % copper plot (Figure: 3.3) after 5% copper addition suggests that a similar behaviour may be observed for copper addition greater than 10%. These observations conclude that carbon content affects the role of VCN in densification of copper bearing steels.

VCN being a refractory hard phase is expected to improve the over all hardness of the steel. But this is not observed in the present investigation. With

increasing VCN content in the steel with or without copper in either sintered or heat treated condition the microhardness of any of the phases observed hardly gets affected. One possible explanation for this may be the fact that VCN is not getting dissolved in steel during sintering or heat treatment. Phase diagrams of Fe-V-C and Fe-V-N suggest this possibility, [52]. According to these, VC completely dissolves in iron at the sintering as well as heat treatment temperatures but VN does not dissolve at all. It appears that with increasing VCN addition, the trend is that of VN.
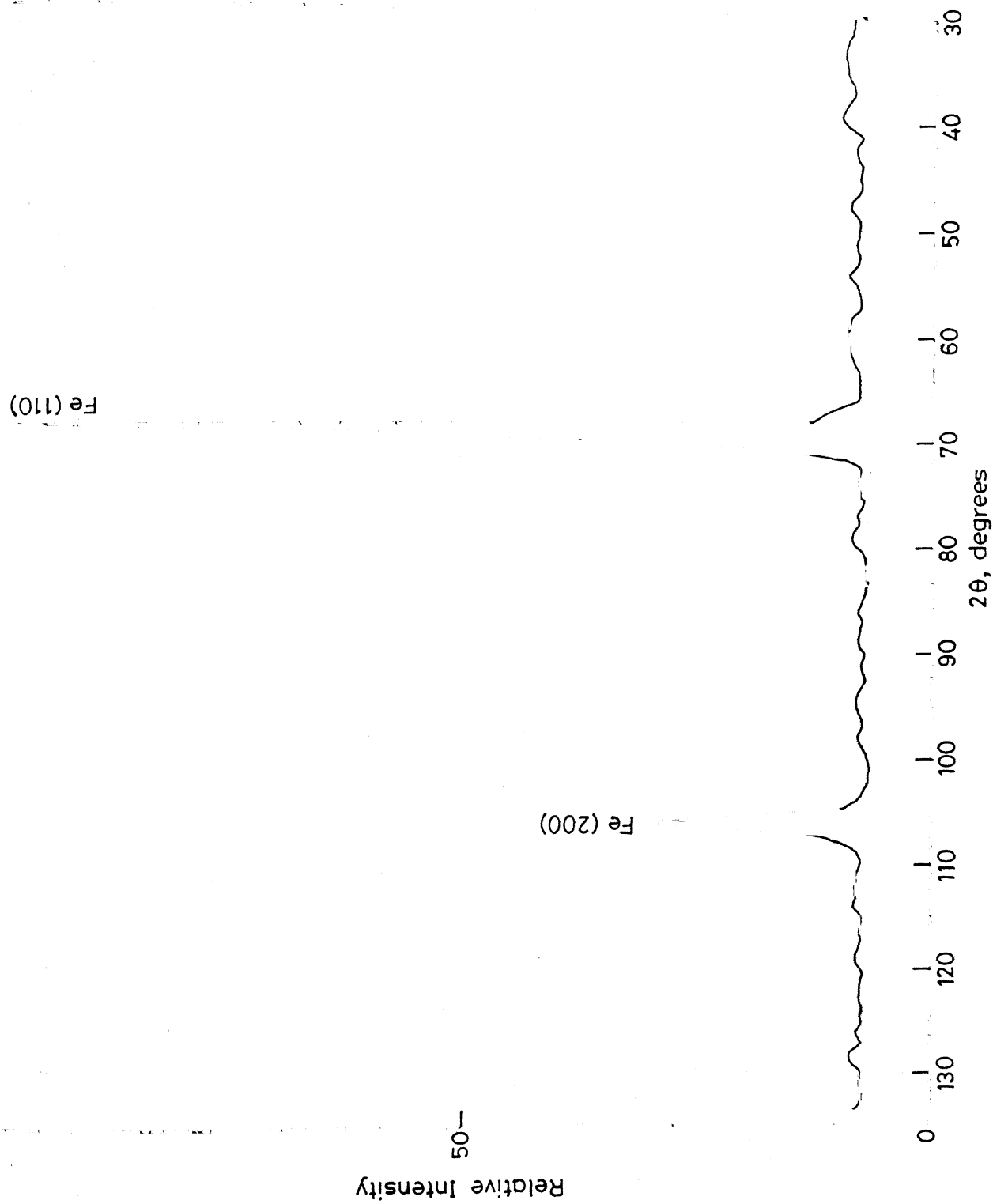
Figure 4.1: XRD plot for 0.5% C- 0.6% VCN-5%Cu steel based on Astaloy A.

Fe (110)

Cu (111)

Cu (200)

Fe (200)

Cu (220)

2θ, degrees

Relative Intensity

30 40 50 60 70 80 90 100 110 120 130
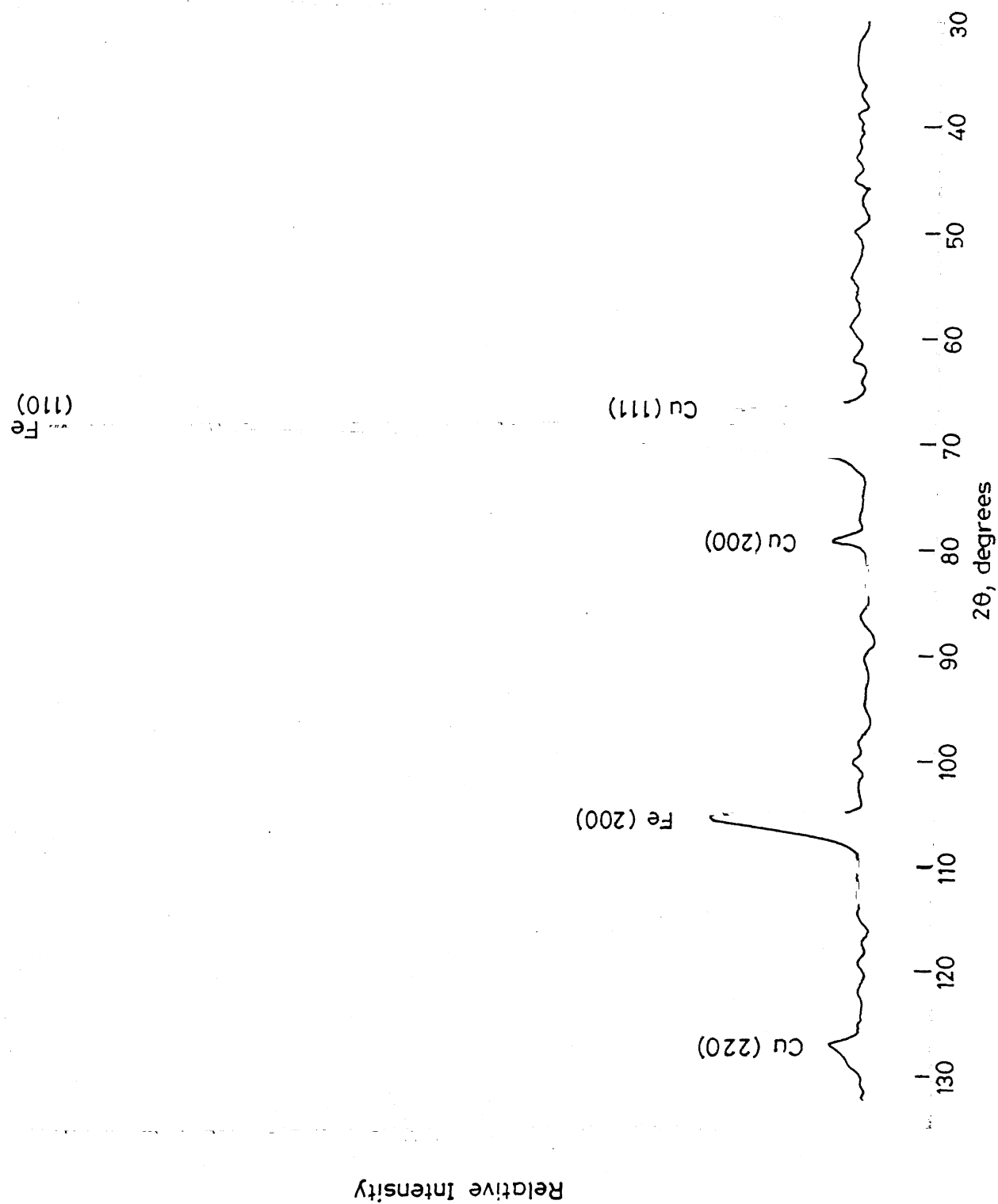
Figure 4.2: XRD plot for 0.5% C, 0.6% V/CN 10% Cu steel based on Astaloy A
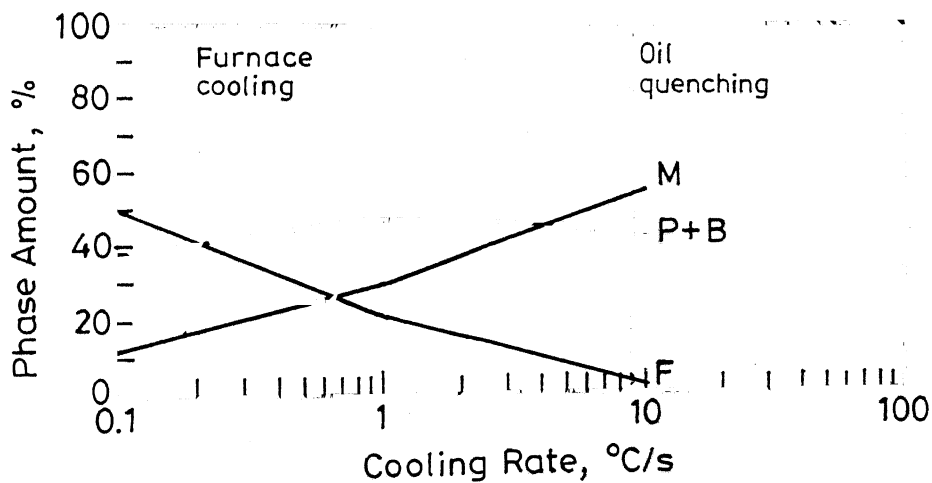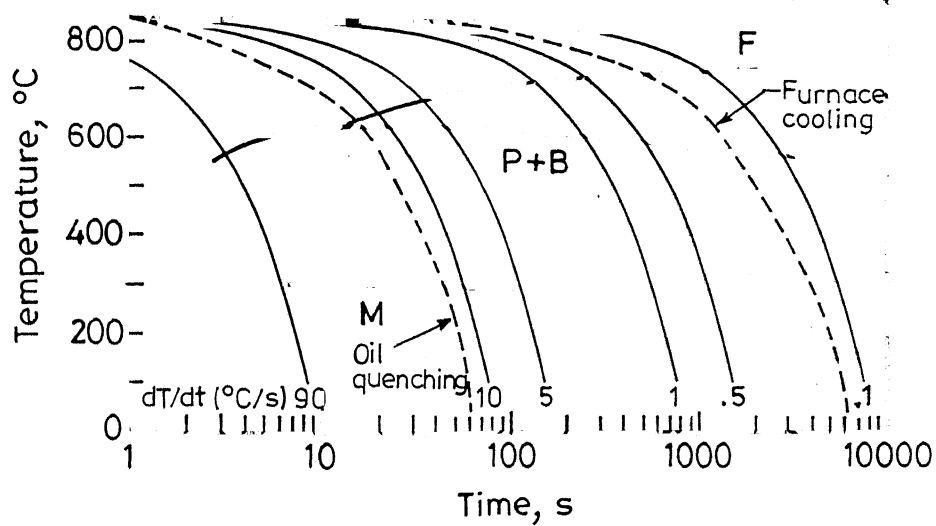
Figure 4.3: Upper: CCT plot for a typical sintered steel (Ni-1.75%, Mo-0.5%,Cu-1.5%,
C-0.45%) based on Distaloy A. [56].

Lower: The variation of various phase contents in the above steel for different
cooling rate. [56].

F   Ferrite
M   Martensite
B   Bainite
P   Pearlite

Chapter 5

Conclusions

Following conclusions can be drawn on the basis of this investigation:

1. Addition of VCN or copper alone in Astaloy A steel causes swelling during sintering. The extent of swelling is directly proportional to their contents. However when both of them are added together the increase in dimension does not follow the same trend. It is expected that VCN particles impede further copper growth during sintering of steels containing higher copper i.e., more than 5%.

2. Dissolution of copper into iron lattice causes expansion in the latter's lattice parameter, which finally results in dimensional growth of compacts during sintering.

3. Addition of copper increases hardenability of the steel which results in increase in hardness with increasing copper content in the steel. At higher copper content i.e., at 10%, the increase in hardness is substantial due to the formation of martensite during oil quenching.

4. Addition of VCN does not affect the hardness of as sintered or heat treated steels as it does not get dissolved in steel either during sintering or heat treatment.

Suggestions for future work

On the basis of present investigation, following suggestions are made for future work in this area:

1) Hot P/M consolidation methods like forging may be tried to further densify the steels.

2) The VCN particles appear to hinder bonding, mainly due to the poor interfacial binding with the matrix. In the presence of Copper the situation appears still worse. Other transition metal additives might be useful, but the negative point there being that a still higher sintering temperature shall be needed.

3) A fine particle size of Copper addition is recommended for lowering the required sintering periods.

4) Use of VC in place of VCN is suggested as VC is expected to dissolve in the steel at the selected sintering temperature which later on during cooling may precipitate as fine VC particles.

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